PHASE FIELD MODEL FOR THE NUCLEATION IN SOLID STATE PHASE TRANSFORMATIONS: THEORIES, ALGORITHMS AND APPLICATIONS

A Dissertation in
Mathematics
by
Lei Zhang

© 2009 Lei Zhang

Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

May 2009
The dissertation of Lei Zhang was reviewed and approved* by the following:

Qiang Du  
Verne M. Willama Professor of Mathematics  
Dissertation Advisor, Chair of Committee

Long-qing Chen  
Professor of Materials Science and Engineering

Chun Liu  
Professor of Mathematics

Xiantao Li  
Assistant Professor of Mathematics

Ludmil Zikatanov  
Associate Professor of Mathematics

John Roe  
Professor of Mathematics  
Head of the Department of Mathematics

*Signatures are on file in the Graduate School.
Abstract

Nucleation takes place when a material becomes thermodynamically meta-stable with respect to its transformation to a new state or new crystal structure. Very often, the nucleation process dictates the microstructure of a material. Predicting the shape of a critical nucleus in solids has been a long-standing problem in solid state phase transformations. It is generally believed that nucleation in solid is the most difficult process to model and predict.

The main focus of this dissertation is the development of mathematical models and numerical algorithms for various nucleation phenomena in solid state phase transformation. Motivated by a general phase field framework with a diffuse interface description of the phase transformation, we develop a new computational approach to predict the morphology of a critical nucleus in solids under the influence of both interfacial energy anisotropy and long-range elastic interactions. The approach can help us uncover the wealth of fascinating topics in the solid states.

The dissertation is organized as follows: In Chapter 1, we give an overview of the nucleation in the solid states and existing nucleation theories, including the classical nucleation theory and the diffuse interface theory. Then we introduce some numerical methods to compute the saddle point and the Minimum Energy Path (MEP).

In Chapter 2, we investigate a phase-field model for finding the critical nucleus morphology in the homogeneous nucleation of solids. We analyze the mathematical properties of a free energy functional that includes the long-range, anisotropic elastic interactions. Based on a minimax technique and the Fourier spectral implementation, the numerical algorithms is developed to search for the saddle points. We demonstrate that the phase-field model is mathematically well defined and is able to efficiently predict the critical nucleus morphology in elastically anisotropic solids without making \textit{a priori} assumptions.

In Chapter 3, we present numerical simulations of the critical nucleus morphol-
ogy in solid state phase transformations. A diffuse interface model combined with
the minimax technique is implemented to predict the morphology of critical nucleus
during solid to solid phase transformations in both two and three dimensions. We
use a particular example of cubic to cubic transformation within the homogeneous
modulus approximation and study the effect of elastic energy contribution on the
morphology of a critical nucleus. The results show that strong elastic energy inter-
actions may lead to critical nuclei with a wide variety of shapes, including plates,
needles and cuboids with non-convex interfaces. It is found that strong elastic
energy contributions may lead to critical nuclei whose point group symmetry is
below the crystalline symmetries of both the new and the parent phases.

In Chapter 4, we develop a constrained string method to solve the saddle-point
problem with general constraints. Based on the description of the string method,
a smooth curve is evolved with intrinsic parametrization whose dynamics takes the
string to the most probable transition path between two metastable regions in con-
figuration space. Then Lagrange multiplier is applied for the extra constraint and
numerical algorithm of the constrained string method is implemented to find the
constrained MEP and saddle points. Numerical analysis includes the conservation
of the constraint and the energy law. We also propose a simplified approach to
implement the constraint by the Augmented Lagrangian method.

By using the constrained string method, we investigate the morphological evo-
lution during precipitation of a second-phase particle in a solid along the entire
transformation path from nucleation to equilibrium in Chapter 5. We show that
a combination of diffuse-interface description and a constrained string method is
able to predict both the critical nucleus and equilibrium precipitate morphologies
simultaneously without a priori assumptions. Using the cubic to cubic transfor-
mation as an example, it is demonstrated that the maximum composition within
a critical nucleus can be either higher or lower than that of equilibrium precipitate
while morphology of an equilibrium precipitate may exhibit lower symmetry than
the critical nucleus resulted from elastic interactions.

In Chapter 6, we present more applications for the nucleation in solids, includ-
ing cubic to tetragonal transformation, and nucleation for two order parameters
in solids. Our works on the mathematical modeling and computational algorithms
open some new research directions and provide useful tools for the analysis of the
nucleation phenomenon in general, for instance, we will consider the dynamic sim-
ulation of the nucleation process, inhomogeneous nucleation, and heterogeneous
nucleation in the near future.
Table of Contents

List of Figures ix

List of Tables xi

Acknowledgments xii

Chapter 1
Overview 1
1.1 Nucleation in solid state phase transformation . . . . . . . . . . . . 1
1.2 Existing theories for nucleation . . . . . . . . . . . . . . . . . . . 2
  1.2.1 Classical nucleation theory . . . . . . . . . . . . . . . . . . . 2
  1.2.2 Phase field model . . . . . . . . . . . . . . . . . . . . . . . . 2
1.3 Numerical methods to find saddle points . . . . . . . . . . . . . . . 4
  1.3.1 Minimax method . . . . . . . . . . . . . . . . . . . . . . . . 5
  1.3.2 String method . . . . . . . . . . . . . . . . . . . . . . . . . 6
  1.3.3 Nudged elastic band method . . . . . . . . . . . . . . . . . . 7
1.4 Content of the thesis work . . . . . . . . . . . . . . . . . . . . . . 8

Chapter 2
Phase field model to critical nuclei in solids 12
2.1 Introduction . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 12
2.2 Classical nucleation theory . . . . . . . . . . . . . . . . . . . . . . 13
2.3 Phase field model . . . . . . . . . . . . . . . . . . . . . . . . . . 15
  2.3.1 Chemical free energy and interfacial energy . . . . . . . . . . . 15
  2.3.2 Elastic energy . . . . . . . . . . . . . . . . . . . . . . . . . 16
2.4 Saddle points . . . . . . . . . . . . . . . . . . . . . . . . . . . . 19
  2.4.1 Existence . . . . . . . . . . . . . . . . . . . . . . . . . . . . 19
Chapter 3
Simulation of critical nucleus morphology in solid-state phase transformations
3.1 Introduction ........................................ 30
3.2 Diffuse Interface Model .......................... 33
3.3 Numerical Algorithm ............................ 35
3.4 2D critical nucleus morphology in solid state transformations .... 37
  3.4.1 Anisotropic interfacial energy ............... 37
  3.4.2 Anisotropic elastic energy contribution .... 38
  3.4.3 Critical nucleus with diffuse interface ...... 39
  3.4.4 2D most probable nucleus morphology .... 39
  3.4.5 More discussions and validations .......... 40
3.5 3D critical nucleus morphology in solid state transformations .... 41
  3.5.1 Anisotropic elastic energy contribution .... 41
  3.5.2 3D most probable nucleus morphology ...... 42
  3.5.3 Competition between the interfacial and elastic energies in the sharp interface limit .... 44
3.6 Conclusion ........................................ 45

Chapter 4
Constrained string method and its numerical analysis 48
4.1 Introduction ........................................ 48
4.2 String method ..................................... 49
4.3 Constrained String Method ...................... 51
  4.3.1 Lagrange Multiplier ......................... 52
  4.3.2 Energy Law .................................. 53
  4.3.3 Illustrative Example ....................... 54
4.4 Discretization of constrained string method ............. 57
  4.4.1 Time-discretized constrained string method 57
  4.4.2 Illustrative example ..................... 58
  4.4.3 Augmented Lagrangian method ............. 59
4.5 Numerical Simulations ........................... 60
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5.1</td>
<td>Algorithm of constrained string method</td>
<td>60</td>
</tr>
<tr>
<td>4.5.2</td>
<td>3D example</td>
<td>61</td>
</tr>
<tr>
<td>4.5.3</td>
<td>Calculation of saddle point by penalty formulation</td>
<td>62</td>
</tr>
<tr>
<td>4.6</td>
<td>Conclusion</td>
<td>64</td>
</tr>
</tbody>
</table>

**Chapter 5**

*Simulation of critical nucleus morphology in the conserved solid field*

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1</td>
<td>Introduction</td>
<td>66</td>
</tr>
<tr>
<td>5.2</td>
<td>Diffuse interface model</td>
<td>69</td>
</tr>
<tr>
<td>5.3</td>
<td>Numerical method</td>
<td>70</td>
</tr>
<tr>
<td>5.3.1</td>
<td>Review of string method</td>
<td>71</td>
</tr>
<tr>
<td>5.3.2</td>
<td>Constrained string method</td>
<td>72</td>
</tr>
<tr>
<td>5.3.3</td>
<td>Time and space discretizations</td>
<td>74</td>
</tr>
<tr>
<td>5.4</td>
<td>Numerical simulations</td>
<td>76</td>
</tr>
<tr>
<td>5.5</td>
<td>Discussion</td>
<td>79</td>
</tr>
<tr>
<td>5.6</td>
<td>Conclusion</td>
<td>81</td>
</tr>
</tbody>
</table>

**Chapter 6**

*More applications and future works*

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1</td>
<td>Critical nucleus for cubic to tetragonal phase transformation</td>
<td>82</td>
</tr>
<tr>
<td>6.1.1</td>
<td>Elastic energy</td>
<td>82</td>
</tr>
<tr>
<td>6.1.2</td>
<td>Discussion of $B(n)$ in 3D</td>
<td>84</td>
</tr>
<tr>
<td>6.1.3</td>
<td>Numerical simulations</td>
<td>86</td>
</tr>
<tr>
<td>6.2</td>
<td>Nucleation for two order parameters in solids</td>
<td>90</td>
</tr>
<tr>
<td>6.2.1</td>
<td>Chemical free energy</td>
<td>90</td>
</tr>
<tr>
<td>6.2.2</td>
<td>Elastic energy for two order parameters</td>
<td>91</td>
</tr>
<tr>
<td>6.2.3</td>
<td>Numerical simulations</td>
<td>95</td>
</tr>
<tr>
<td>6.3</td>
<td>Future works</td>
<td>97</td>
</tr>
<tr>
<td>6.3.1</td>
<td>Dynamic simulation of the nucleation process</td>
<td>97</td>
</tr>
<tr>
<td>6.3.1.1</td>
<td>Langevin force approach</td>
<td>97</td>
</tr>
<tr>
<td>6.3.1.2</td>
<td>Explicit nucleation algorithm</td>
<td>98</td>
</tr>
<tr>
<td>6.3.1.3</td>
<td>Numerical simulation</td>
<td>100</td>
</tr>
<tr>
<td>6.3.2</td>
<td>Inhomogeneous nucleation in solid states</td>
<td>101</td>
</tr>
<tr>
<td>6.3.2.1</td>
<td>Mechanical equilibrium equation</td>
<td>101</td>
</tr>
<tr>
<td>6.3.2.2</td>
<td>Iterative-perturbation scheme</td>
<td>103</td>
</tr>
<tr>
<td>6.3.2.3</td>
<td>Coupling with the phase field simulation</td>
<td>104</td>
</tr>
<tr>
<td>6.3.3</td>
<td>Heterogeneous nucleation in solid states</td>
<td>104</td>
</tr>
<tr>
<td>6.3.3.1</td>
<td>Elastic field of a dislocation</td>
<td>105</td>
</tr>
</tbody>
</table>
6.3.3.2 Phase field description of a binary system with dislocation ........................................ 106
6.3.4 Summary .................................................................................................................. 107

Bibliography ..................................................................................................................... 108
List of Figures

2.1 Double well potentials with driving forces $\lambda=0.1, 0.3$ .......................... 16
2.2 Plots of critical nuclei for $\epsilon=1/32$ .............................................. 27
2.3 Logarithms of the $H^1$ errors for $\epsilon = 1/32$ and $1/64$. ....................... 28
2.4 Plots of critical nuclei for $\epsilon=2/N$ with $N=64, 128, 256, 512$. .......... 29

3.1 Double well potential ................................................................. 34
3.2 Critical nuclei with $\alpha_y/\alpha_x = 1.3$ and $\beta = 0$, and nuclei in the
  cubically anisotropic system with $\beta = 0.2, 0.8, 1.2$ and $\alpha_y/\alpha_x = 1$. 38
3.3 Critical nuclei with $\alpha_y/\alpha_x = 1.3$ and $\beta = 0$, and nuclei in the
  cubically anisotropic system with $\beta = 0.2, 0.8, 1.2$ and $\alpha_y/\alpha_x = 1$. 38
3.4 Critical nuclei with diffuse interface width $0.06, 0.1$ and $0.15$. .......... 39
3.5 Critical nucleation energy with changing elastic energy contribution
  and critical nuclei profiles. .......................................................... 40
3.6 Local energy surface near non-convex nucleus and a comparison of
  energies for rectangular nuclei. .................................................. 41
3.7 3D saddle point profiles for $\beta = 0, 0.63, 1.25$ .................................. 42
3.8 3D saddle point profiles in plate and needle shapes for $\beta=0.31, 0.94,$
  $1.56$ .................................................. 42
3.9 Critical nucleation energy with changing driving force (left) and
  changing elastic energy contribution (right). ............................ 43
3.10 Surface of elastic energy (left) and surface energy (right) for the
  cuboid nuclei. .................................................................. 45
3.11 Surface and elastic energies and their various combinations. .......... 46

4.1 the exact MEP (left) and the calculated constrained MEP (right),
  $N = 30$ .......................................................... 62
4.2 error(N) of the calculated MEP vs N. .......................................... 63

5.1 Free energy increase for $c_0=1, -0.9$ and $c_s$. .............................. 69
5.2 Change computational domain .................................................. 75
5.3 Critical nucleus, equilibrium and MEP for $c_0 = -0.9$ ................. 77
5.4 Critical nucleus, equilibrium and MEP for $c_0 = -0.88$ .......................... 77
5.5 composition profile of critical nucleus and equilibrium solution along $x$ direction, $c_0 = -0.9$ (left) and $c_0 = -0.88$ (right) .......................... 78
5.6 the calculated MEPs for $\beta = 0.5, 1, 1.5$. The critical nuclei and equilibrium solutions are inserted. .......................... 78
5.7 the convergence of the Lagrange multiplier for the penalty method: saddle point (red curve) and equilibrium solution (blue curve) .... 79
5.8 Critical nucleation energy with changing driving force (left), MEP with elasticity for $c_0 = -0.93$ and without elasticity for $c_0 = -0.945$ (right) ................................................................. 81

6.1 $\epsilon_{11} = 3, \epsilon_{33} = 1, c_{44} = 50$(left) and $c_{44} = 100$(right) ..................... 86
6.2 $\epsilon_{11} = 1, \epsilon_{33} = 3, c_{44} = 50$(left) and $c_{44} = 100$(right) ..................... 86
6.3 $\epsilon_{11} = 1, \epsilon_{33} = -2, c_{44} = 50$(left) and $c_{44} = 100$(right) ..................... 86
6.4 Critical nucleus, equilibrium and MEP for $\beta = 1.$ ............................................ 89
6.5 Critical nucleus, equilibrium and MEP for $\beta = 2.5.$ ........................................ 89
6.6 Critical nucleus, equilibrium and MEP for $\beta = 3.$ ............................................ 89
6.7 Free energy surface, contour, free energy for one single domain ... 91
6.8 Critical nucleus and equilibrium state for $\beta = 0$ ............................................. 96
6.9 Critical nucleus and equilibrium state for $\beta = 0.5$ ........................................ 96
6.10 Critical nucleus and equilibrium state for $\beta = 0$ ............................................ 96
6.11 Critical nucleus and equilibrium state for $\beta = 1$ ............................................ 97
6.12 Nucleation and growth process at time $t = 20, 100$ and $190$ .... 101
List of Tables

2.1 Errors of Fourier spectral solutions for changing $\epsilon$ . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 28

5.1 Composition profile of the equilibrium solution for $n = 128$ and $n = 256$ . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 80
Acknowledgments

First of all, it is my great honor to have Prof. Qiang Du, the Verne M. Willaman Professor in the Department of Mathematics, as my advisor. I am greatly indebted to him for all the guidance, inspiration, patience and encouragement he provided me not only for my work but also in daily life over the years. He is the best advisor and the best friend I could ever ask for.

I am deeply grateful to Prof. Long-qing Chen in the Department of Material Science and Engineering for his kindness and help on my thesis work. His enlightening discussions have been numerous valuable.

I would like to thank my Committee Members, Prof. Chun Liu, Prof. Ludmil Zikatanov and Prof. Xiantao Li, for their insightful commentary on my work.

I would also like to thank all the colleagues of my group: Jian Zhang, Tianjiang Li, Manlin Li, Yanxiang Zhao, Thinh Le, Yanping Ma, Kun Zhou, Jingyan Zhang with whom I had many helpful discussions during our group meetings.

I have been supported by a number of NSF grants awarded to Prof. Qiang Du. I have received financial support from the Department of Mathematics at the Pennsylvania State University, including a Pritchard Dissertation Fellowship.

I am very grateful for my parents and my brother, and I especially want to thank my wife, Zhenzhen Zheng, for her love, constant support and encouragement so that I can make me get this work through.

Finally, my thanks go to those who, directly or indirectly, helped me finish my thesis.
Overview

1.1 Nucleation in solid state phase transformation

One of the most efficient approaches to design the properties of a material is through the control of its phase transformations and microstructure evolution. The processes involved in a phase transformation are inherently multiscale. It starts with the nucleation of nanoscale nuclei of new phase particles, followed by growth and particle impingement or coarsening.

Nucleation is a very common physical phenomenon in nature. It takes place when a material becomes meta-stable during its transformation to a new state (solid, liquid and gas) or new crystal structure. The nucleation process dictates the microstructure of a material. Predicting the shape of a critical nucleus in solids has been a long-standing problem in solid-state phase transformations. Nucleation in a solid typically involves not only compositional changes but also structural changes. Moreover, interfacial energy is usually anisotropic, and the elastic energy contribution arising from the lattice mismatch between nuclei and matrix plays an important role in determining the morphology of critical nuclei.

We have developed a new computational tool based on the phase-field description to predict the morphology of critical nuclei in the solid state phase transformation under the influence of both interfacial energy anisotropy and long-range elastic interactions [75, 76, 77, 78], which helped us uncover the wealth of fasci-
nating research topics associated with this field [79, 80, 81].

1.2 Existing theories for nucleation

1.2.1 Classical nucleation theory

One popular approach to study nucleation is based on the classical nucleation theory developed in 1930s. It is still the most often used theory in studying nucleation as of today [11, 14, 24]. The earlier studies mostly considered phase changes in fluids such as a liquid droplet in a vapor phase. It was then natural to adopt spherical shapes for the critical nuclei. The thermodynamic properties of a nucleus are assumed to be uniform and the same as in the corresponding bulk phase at equilibrium. The interface between a nucleus and the parent phase is considered to be sharp. The calculation of a critical nucleus size is then determined by the competition between the bulk free energy reduction and interfacial energy increase. A nucleation event takes place by overcoming the minimum energy barrier which leads to the critical size of the nucleus obtained as a stationary point of the energy. Despite the assumption of spherical shapes for critical nuclei, the same classical theories have been utilized to interpret kinetics of many phase transformations involving solids including solid to solid transformations. As a matter of fact, for some systems, the classical nucleation theory has been shown to provide a good description on the nucleation kinetics.

1.2.2 Phase field model

Another theoretical approach to nucleation is based on the phase field (diffuse interface) description, also called the non-classical nucleation theory. In this approach, the properties within a nucleus are inhomogeneous and the interface between the nucleus and parent matrix is diffuse.

A phase field model describes a microstructure, both the compositional/structural domains and the interfaces, as a whole by using a set of field variables. The field variables are continuous across the interfacial regions, and hence the interfaces in a phase field model are diffuse. There are two types of field variables, conserved and nonconserved. Conserved variables have to satisfy the local conser-
vation condition. In the diffuse interface description, the total free energy of an inhomogeneous microstructure system described by a set of conserved \( c_1, c_2, \ldots \) and nonconserved \( \eta_1, \eta_2, \ldots \) field variables is then given by

\[
E = \int \left[ f(c_1, c_2, \ldots, c_n, \eta_1, \eta_2, \ldots, \eta_m) + \sum_{i=1}^{n} \alpha_i (\nabla c_i)^2 \right. \\
+ \left. \sum_{i=1}^{3} \sum_{j=1}^{3} \sum_{k=1}^{m} \beta_{ij} \nabla_i \eta_k \nabla_j \eta_k \right] dx + \int \int G(x - x') dx dx' \tag{1.2}
\]

where \( f \) is the local free-energy density that is a function of field variables \( c_i \) and \( \eta_i \), \( \alpha_i \) and \( \beta_{ij} \) are the gradient energy coefficients. The first volume integral represents the local contribution to the free energy from short-range chemical interactions. The origin of interfacial energy comes from the gradient energy terms that are nonzero only at and around the interfaces. The second integral represents a nonlocal term that contains the contributions to the total free energy from any one or more of the long-range interactions, such as elastic interactions, electric dipole-dipole interactions, electrostatic interactions, etc., that also depend on the field variables. The main differences among different phase field models lie in the treatment of various contributions to the total free energy.

Cahn and Hilliard [6] developed a continuum model taking into account the diffuse nature of interfaces, and studied the composition profiles of a critical nucleus, as a function of matrix composition from close to its equilibrium composition \( c_\alpha \), to the spinodal composition \( c_s \). They found that, for matrix compositions near \( c_\alpha \), the composition within a critical nucleus was almost identical to that of the equilibrium precipitate phase \( c_\beta \). As the matrix composition increases from \( c_\alpha \), the profiles of a critical nucleus became increasingly diffuse, with the composition within the nucleus approaching that of the matrix. Based on this study, they concluded that classical nucleation, which required the nucleus composition to be uniform and equal to \( c_\beta \), was operative only when the matrix composition of the alloy was close to \( c_\alpha \). They also found that the radius of the critical nucleus diverged to infinity not only near \( c_\alpha \), as predicted by the classical nucleation theory, but also near \( c_\beta \).

More recently, LeGoues et al. [48] used a discrete lattice model [5] to calculate
the profiles of the occupation probabilities (which refer to the probability that a
given lattice site is occupied by an atom of a given type) for a critical nucleus, and
found that at high temperatures and low supersaturations their profiles matched
very well with those obtained using the Cahn-Hilliard continuum model. Only at
intermediate compositions are there some differences between the profiles obtained
from the continuum and discrete models. They found qualitative agreement with
the continuum model for the variation of the radius of the critical nucleus with
composition, as well.

Roy et al [63] discussed the nucleation in the presence of a general long-range
interaction, focusing on the critical order parameter profiles rather than predicting
the morphology of a nucleus. Wang and Khachaturyan [72] examined the morphol-
ogy of nuclei during a martensitic transformation by switching on and off Langevin
noise. The particles obtained using this approach do not necessarily correspond
to saddle point configurations associated with a critical nucleus. Poduri and Chen
[59] studied the nucleation of an ordered precipitate from a disordered matrix by
extending the diffuse-interface theory of Cahn and Hilliard. Chu et al [10] explored
the nucleation of martensites using a diffuse-interface phase model. More recently,
Gagne et al [26] studied the morphological evolution using Langevin simulations of
martensitic transformations in two dimensions. They concluded that systems with
long-range interactions quenched into a metastable state near the pseudospinodal
exhibit nucleation that is qualitatively different from classical nucleation near the
coexistence curve. It is noted that all existing diffuse interface theories for nu-
cleation in solids largely ignore the anisotropic interfacial energy and anisotropic
long-range elastic interactions.

1.3 Numerical methods to find saddle points

A large spectrum of phenomena for finding the saddle point include conformational
changes in macromolecules, chemical reactions to diffusion in condensed-matter
systems and nucleation events during phase transformations. Methods for finding
saddle points prove to be more challenging than those for finding minima because
saddle point is unstable. A large variety of ideas have already been proposed
on this topic, including minimax method [12, 51, 52, 60], string method [18, 19],
nudged elastic band method [33, 34, 35], dimer method [36], etc.

1.3.1 Minimax method

The minimax technique has been studied extensively in calculus of variation and optimization which is based on the mountain pass theorem [60]. Various minimax theorems have been successfully established to prove the existence of multiple solutions to various nonlinear PDEs and dynamic systems [3, 53]. Most minimax theorems in the literature mainly focus on the existence issue. They require one to solve a two-level global optimization problem, i.e., (constrained) global maximizations at the first level and a global minimization at the second level, and therefore are not for algorithm implementation. Choi and McKenna [12] proposed a numerical minimax algorithm, called a mountain pass method, to solve the model problem basically for a solution with Morse Index is 1. The algorithm opens a brand new door to numerically compute unstable solutions.

Li and Zhou [51] developed a new minimax method for finding multiple saddle points in 2001. The method is applied to solve the semilinear Boundary Value problem:

\[ \triangle u(x) - lu(x) + f(x, u(x)) = 0, \quad x \in \Omega \quad (1.3) \]

for \( u \in H \) with either the zero Dirichlet boundary condition or the zero Neumann boundary condition, where \( \Omega \) is a bounded open domain in \( \mathbb{R}^N \), and \( f \) is a nonlinear function of \( (x, u(x)) \) with \( u \in H \) (\( H \) is a Banach space). The associated variational functional is the energy

\[ E(u) = \int_{\Omega} \left[ \frac{1}{2} |\nabla u(x)|^2 + \frac{1}{2} lu^2(x) - F(x, u(x)) \right] dx \quad (1.4) \]

where \( F(x, t) = \int_0^t f(x, \tau) d\tau \).

The main idea of the minimax algorithm for finding saddle points is listed as follows:

1. First define a solution (stable) submanifold \( \mathcal{M} \) s.t. a local minimum point of \( E(u) \) on \( \mathcal{M} \) yields a critical point. Thus the problem becomes a minimization of \( E(u) \) on the submanifold \( \mathcal{M} \), and a saddle point becomes stable on the submanifold \( \mathcal{M} \). If a monotone decreasing search is used in the min-
imization process, the algorithm will be stable. At a point on \( M \), we can apply, e.g., a steepest descent search to approximate a local minimizer of \( E(u) \) on \( M \).

2. There must be a *return rule*. As a steepest descent search usually leaves the submanifold \( M \), for the algorithm to continue to iterate we need to design a return rule for the search to return to \( M \).

3. There must be a strategy to *avoid degeneracy*. Since we are searching for a saddle point at a higher critical level, at least, for a new solution, a simple minimization may cause degeneracy is crucial to guarantee that the new critical point found is different from the old ones.

In [51], the numerical minimax algorithm is implemented successfully to solve a class of semilinear elliptic boundary value problems for multiple solutions on some nonconvex, non star-shaped and multiconnected domains. Some convergence Results of the algorithm are presented in [52].

### 1.3.2 String method

The string method is developed by E. Ren and Vanden-Eijnden [18, 19]. The main objective of the string method is to find the Minimum Energy Path (MEP) and saddle points for barrier-crossing events. The method proceeds by evolving strings, i.e., smooth curves with intrinsic parametrization whose dynamics takes them to the most probable transition path between two metastable regions in configuration space. It has become widely used for estimating transition rates within the transition state theory approximation [25].

Assuming that the potential energy \( E(x) \) has at least two minima, at \( a \) and \( b \). By definition, a MEP is a smooth curve \( \varphi^* \) connecting \( a \) and \( b \) that satisfies

\[
(\nabla E)^\perp(\varphi^*) = 0
\]

where \( \nabla E(\varphi) \perp \) is the component of \( \nabla E(\varphi) \) normal to \( \varphi \),

\[
(\nabla E)^\perp(\varphi) = \nabla E(\varphi) - (\nabla E(\varphi), \hat{\tau})\hat{\tau}.
\]
Here $\hat{\tau}$ is the unit tangent of the curve $\varphi$ and $\langle \cdot, \cdot \rangle$ denotes the inner product in the Euclidean space.

In [18], the string method uses $\varphi(\alpha, t)$ to denote the instantaneous position of the string ($\alpha$ is some suitable parametrization). Then the MEP can be found by solving the following dynamics equation:

$$\varphi_t = -(\nabla E)^\perp(\varphi) + \lambda \hat{\tau}, \quad (1.6)$$

where $\hat{\tau} = \frac{\varphi_{\alpha}}{|\varphi_{\alpha}|}$, and the scalar field $\lambda \equiv \lambda(\alpha, t)$ is a Lagrange multiplier uniquely determined by the choice of parametrization.

One of the computational complexity is the calculation of the projected force. It needs to compute the tangent vector by different ways before and after the saddle point is crossed to ensure the numerical stability, which may lower the accuracy of the method. In [19], a simplified and improved string method is proposed to eliminate the projection step, i.e.,

$$\varphi_t = -\nabla E(\varphi) + \bar{\lambda} \hat{\tau}, \quad (1.7)$$

where $\bar{\lambda}$ is still a Lagrange multiplier to enforce the particular parametrization of the string, which is equivalent to (5.6) with $\bar{\lambda} = \lambda + (\nabla E(\varphi), \hat{\tau})$.

The simplified string method shows the advantage of the numerical computations. The algorithm becomes more stable and more accurate.

### 1.3.3 Nudged elastic band method

The Nudged Elastic Band (NEB) method [33, 35, 36] is another efficient method for finding the MEP between a given initial and final state of a transition. The discrete representation of a string is created and connected together with springs. An optimization algorithm is then applied to relax the string down towards the MEP. The total force on each point $x_i$ on the string contains the spring force along tangent and the true force perpendicular to the tangent:

$$F_i = -(\nabla E)^\perp(x_i) + (F_i^s)^\parallel \quad (1.8)$$
where, in the simplest version of the method, the spring force is evaluated as

\[(F^s_i)\| = k[(x_{i+1} - x_i) - (x_i - x_{i-1})] \cdot \hat{\tau}_i \hat{\tau}_i.\]

\(k\) is the spring constant. The unit tangent vector \(\hat{\tau}_i\) is estimated by

\[\hat{\tau}_i = \frac{x_{i+1} - x_{i-1}}{|x_{i+1} - x_{i-1}|}.\]  

(1.9)

An improved way of estimating the local tangent in the NEB method for finding MEP is presented in [35]. This eliminates a problem which occurred in systems where the force parallel to the MEP was very large compared with the restoring force perpendicular to the MEP. In such situations kinks could form on the elastic band and prevent rigorous convergence to the MEP.

While the NEB method gives a discrete representation of the MEP, the energy of saddle points needs to be obtained by interpolation. When the energy barrier is narrow compared with the length of the MEP, few images land in the neighborhood of the saddle point and the interpolation can be inaccurate. In [36], Henkelman et al described a climbing image NEB method for finding saddle points and MEP. One of the images is made to climb up along the elastic band to converge rigorously on the highest saddle point. Also, variable spring constants are used to increase the density of images near the top of the energy barrier to get an improved estimate of the reaction coordinate near the saddle point.

### 1.4 Content of the thesis work

In Chapter 2, we investigate a phase field model for homogeneous nucleation and critical nucleus morphology in solids. We analyze the mathematical properties of a free energy functional that includes the long-range anisotropic elastic interactions. We describe the numerical algorithms for searching the saddle points of such a free energy functional based on the minimax technique and the Fourier spectral implementation.

In Section 2.1, we first describe the background of nucleation in solids and phase field model. Then in Section 2.2, we introduce the classical nucleation theory in
fluids, why the nucleation in solids is much more complicated than that in fluids, and prior application of the classical nucleation theory to solids. In Section 2.3, we present a new approach for predicting the morphology of a critical nucleus as an extreme state in two dimensions by considering the presence of both interfacial energy anisotropy and elastic interactions. In Section 2.4, mathematical analysis of saddle points is presented. To study the existence theory of saddle points, we first show that the energy functional given by phase field model satisfies the Palais Smale condition. Then we apply the mountain pass theory to prove the existence theorem of saddle point. We also introduce the $\Gamma$-convergence for saddle point of the Ginzburg-Landau like functional, which is often computed via direct geometric modeling of the zero level set of phase field variable. In Section 2.5, we derive the Euler-Lagrange equation by the calculus of variation. We then have a general error estimate of Fourier spectral approximation. Furthermore, we present a numerical algorithm which adopts the minimax technique to find the saddle points. In Section 2.6, we conduct a series of numerical experiments in two dimensions to verify the spectral accuracy of the computed solution. Then we present an example to illustrate that the solution is convergent to a sharp interface solution.

In Chapter 3, we present numerical simulation of critical nucleus morphology in solid state phase transformations. A diffuse interface model combined with the minimax technique is implemented in both two and three dimensions. It is demonstrated that the morphology of critical nuclei in cubically anisotropic solids can be efficiently predicted by the computational model without a priori assumptions.

In Section 3.1, we give an introduction of nucleation in solids and overview the existing works and different approaches to study various nucleation phenomena. In Section 3.2 and 3.3, we review the diffuse interface model and numerical algorithm. In Section 3.4, a number of two-dimensional numerical simulations are carried out in order to make predictions on the critical nucleus morphologies based on the developed model and the numerical algorithm. It indicates that the morphology of a critical nucleus, or a critical fluctuation in elastically anisotropic solids can be successfully predicted by a combination of the diffuse-interface approach and the minimax algorithm. Then we analyze the most probable nucleus morphology for a given relative elastic energy and chemical driving force contributions. Our calcu-
lations reveal the fascinating possibility of nuclei with non-convex shapes, as well as the phenomenon of shape-bifurcation and the formation of critical nuclei whose symmetry is lower than both the new phase and the original parent matrix. In Section 3.5, we extend the numerical algorithm to three dimensional computation. Numerical results show that the critical nuclei could be cuboidal, plate or needle shape. More comparisons of the various energy contributions offer us additional insights into the numerically observed phenomena via some analytical calculations in the sharp interface limit.

In Chapter 4, we develop a constrained string method to solve the saddle-point problem on the general constrained manifold. Numerical algorithm is implemented to find the constrained MEP and saddle points. We show numerical analysis including the conservation of the constraint and the energy law. Moreover, time-discretization for the constrained string method is analyzed and nice approximation features are presented.

In Section 4.1, we give a brief introduction of some popular numerical methods for finding the MEP and saddle points, and describe variant approaches to solve the constrained problems. In Section 4.2, we review the original string method and its dynamics. Then a simplified version of string method is also presented. In Section 4.3, a constrained string method is developed to find the MEP and saddle point on general constrained manifold. A Lagrange multiplier is applied to the original string method, and energy law and an illustrative example are discussed. In Section 4.4, time discretization of the constrained string method is presented, and we use a Ginzburg-Landau energy as an illustrative example. Then, we implement the constraint by augmented Lagrangian method, and numerical algorithm is given. In Section 4.5, some numerical simulations are carried out to test the constrained string method. A detailed numerical algorithm is described, then we use a 3D example to illustrate the developed method and numerical convergence is presented. Moreover, we compare the saddle-point calculation by penalty formulation. It shows that the string method with the penalty formulation can overcome the flaw of the penalty method. Final conclusion is made in Section 4.6.

In Chapter 5, we develop a new approach to solve the nucleation problems in the conserved solid field by using the constrained string method. We combine the phase field model with the constrained string method to find the critical nu-
cleus and equilibrium solution simultaneously with the effect of the elastic energy contributions.

In Section 5.1, we introduce the background of nucleation in solids and recent progress on predicting the morphology of critical nuclei in solids. Then we extend our study in a non-conserved field to a conserved field. In Section 5.2, a diffuse interface model is developed and a composition profile is used in the conserved field. In Section 5.3, we first review the original string method, and then describe the constrained string method we developed in the previous Chapter. Meanwhile, time and space discretizations are made by using FFT and some other techniques. In Section 5.4, we present some numerical simulations to compute both the critical nucleus and equilibrium solution with a conserved composition parameter based on the developed model and the numerical algorithm. Some two-dimensional examples show that both the critical nucleus and the equilibrium solution could be cubic or plate shapes which depend on the elastic energy contributions. It reveals that the morphology of a critical nucleus can be drastically different from the equilibrium solution due to the elastic energy contributions. Furthermore, a series of numerical experiments are also conducted to verify the convergence of the constrained string method. More discussion are presented in Section 5.5. We investigate the profile of equilibrium solution without elasticity for different average composition, plot the critical free energy as a function of average composition, and also compare the results with the case of the non-conserved field. Then we give a final conclusion in Section 5.6.

In Chapter 6, we present some on-going works, including cubic to tetragonal transformation, and nucleation for two order parameters in solids. Our works on the mathematical modeling and computational algorithms opened some new research directions and provided useful tools for the analysis of the nucleation phenomenon in general, for instance, we will consider inhomogeneous nucleation, dynamic simulation of the nucleation process, and heterogeneous nucleation in the near future.

Parts of this thesis work have been reported in several publications [75, 76, 77, 78].
2.1 Introduction

Nucleation refers to a process that takes place when a material becomes metastable with respect to its transformation to a new state (solid, liquid, and gas) or new crystal structure. Predicting nucleation rate and its dependence on composition/temperature is critical for controlling the microstructure of a material and thus its properties.

Phase-field methods have been extensively applied to modeling microstructure evolution for various materials processes including solidification, solid state phase transformations, grain or phase coarsening, etc [7]. They have also been used in fluid mechanics, biomechanics and other settings [1, 16]. The diffuse interface (phase field) approach is an attractive and popular tool in materials science simulation and design since the evolution of different microstructural features can be predicted by means of a single set of equations, and there are no explicit boundary conditions defined at interfaces.

In this Chapter, we investigate a phase-field model for homogeneous nucleation and critical nucleus morphology in solids. We analyze the mathematical formulation of the diffuse-interface description of a critical nucleus and the numerical algorithms obtaining the critical order parameter profiles. In particular, we discuss
the existence of saddle points, the minimax algorithm, and the Fourier spectral approximations. We also present numerical examples to illustrate the effectiveness of the computational and modeling approach. It is demonstrated that the phase-field model is mathematically well defined and is able to efficiently predict the critical nucleus morphology in elastically anisotropic solids without making \textit{a priori} assumptions.

### 2.2 Classical nucleation theory

The classical nucleation theory was first developed in 1930s. It is still the most often used theory in studying nucleation as of today. The earlier studies mostly considered phase changes in fluids such as a liquid droplet in a vapor phase. It was then natural to adopt spherical shapes for the critical nuclei. The thermodynamic properties of a nucleus are assumed to be the same as in the corresponding bulk phase. The calculation of a critical spherical droplet in a supersaturated exterior phase is then performed, with the size of a critical nucleus being determined as a result of competition between the bulk free energy reduction and interfacial energy increase. For instance, the free energy change accompanying the formation of a new particle can be given by

\[
\Delta G = V \Delta g + A \cdot \gamma
\]

where \( V \) is volume of particle, \( A \) is surface area, \( \Delta g \) is chemical free energy change per unit volume, \( \gamma \) is the specific interfacial energy. For a spherical particle of radius \( r \),

\[
\Delta G = \frac{4}{3} \pi r^3 \Delta g + 4 \pi r^2 \gamma .
\]

The radius \( r^* \) of the critical nucleus must then be such that

\[
r^* = -\frac{2\gamma}{\Delta g} .
\]

The critical free energy of formation of a critical nucleus, \( \Delta G^* \), is then given by

\[
\Delta G^* = \frac{16\pi \gamma^3}{3(\Delta g)^2} .
\]
Hence, the nucleation rate of the critical nucleus per unit volume and unit time has the form

\[ I = I_0 \exp\left[-\frac{\Delta G^*}{k_B T}\right] \]

where the pre-exponential factor \( I_0 \) calculated from the fundamental statistical approaches, \( k_B \) is the Boltzmann’s constant and \( T \) is the absolute temperature.

The classical theories have been utilized to interpret kinetics of many phase transformations involving solids including solid to solid transformations, and have had some success for providing good descriptions on the nucleation kinetics for some systems, despite the assumption on the spherical critical nuclei shapes. On the other hand, nucleation in solids is generally significantly more complicated than that in fluids. This can be understood from several aspects: first of all, due to the crystallographic nature of most solids, the interfacial energy between a nucleus and the matrix is generally anisotropic, which thus leads to non-spherical minimum surface shapes; meanwhile, there are typically mismatches between the lattice parameters of a new phase and the corresponding parent, so an elastic energy is generated during the nucleation to accommodate such lattice mismatch between a nucleus and the matrix. Since the elastic energy contribution depends on the morphology of a nucleus and lattice mismatch between the nucleus and the matrix, a direct geometric construction of the shape of a critical nucleus is thus very difficult. It is particularly challenging in cases where both elastic energy and surface energy anisotropy exist.

As a result, prior applications of the classical nucleation theory to solid state transformations typically make assumptions on the shape of a nucleus as an \( a \) \textit{prima-ori}, and the elastic energy contribution to nucleation is included as an extra barrier for nucleation, which is proportional to volume, i.e., \( a^* \sim -\beta^* \gamma/(\Delta f_\nu + E_{el}) \) where \( a^* \) represents the critical size of a nucleus, \( \Delta f_\nu \) is the bulk driving force for nucleation, \( \beta^* \) is a numerical factor depending on the shape of the nucleus, and \( E_{el} \) is the elastic strain energy contribution to nucleation on the order of \( C\epsilon_0^2 \) where \( C \) is the elastic modulus and \( \epsilon_0 \) is the lattice mismatch strain (transformation strain, eigenstrain, stress-free strain) between the nucleus and the matrix.
2.3 Phase field model

The non-classical theory was pioneered by Cahn and Hilliard [6]. For subsequent studies, generalization and application to nucleation in solids, we refer to the discussion in the works of [10, 26, 59, 63, 72]. It should be pointed out that these existing diffuse interface theories for nucleation in solids have largely ignored the anisotropic interfacial energy and anisotropic long-range elastic interactions until recently [75].

We now describe the phase field diffuse-interface model considered in [75]. First, as an illustration, only a structural transition is assumed with no compositional changes. It is also assumed that the structural difference between the parent phase and the nucleating phase can be sufficiently described by a single order parameter $\eta$. Extensions to more general cases can also be considered in a similar fashion.

2.3.1 Chemical free energy and interfacial energy

At a given temperature, the chemical free energy dependence on $\eta$ is described by a double-well potential

$$f(\eta) = \frac{1}{4} - \frac{\eta^2}{2} + \frac{\eta^4}{4} - \lambda h(\eta)$$

with local energy wells at $\eta = 1$ and $\eta = -1$ respectively and

$$h(\eta) = \frac{3\eta - \eta^3}{2}$$

so that $2\lambda$ determines the well depth difference which gives the bulk free energy driving force for the phase transformation from the $\eta = -1$ state to the $\eta = 1$ state. In Figure 3.3, $f$ is plotted for two values of $\lambda$.

The total free energy of an inhomogeneous system described by a spatial distribution of $\eta$ is given by:

$$E = \int_{\Omega} (f(\eta) + \frac{1}{2}|M\nabla\eta|^2)dx .$$

Here, the domain $\Omega = (-1,1)^d$ is used with $d$ being the space dimension and a
periodic boundary condition is used for the order parameter \( \eta \). The period should be large compared to the size of the nucleus to avoid edge effects. \( M \) is the gradient energy coefficient which is a constant diagonal tensor in \( \Omega \) for isotropic interfacial energy. For anisotropic interfacial energy, \( M \) may be made either directionally dependent or dependent on the derivatives of \( \eta \).

### 2.3.2 Elastic energy

To incorporate the effect of long-range elastic interactions on the morphology of a critical nucleus, and thus the nucleation barrier, the computation of the elastic energy \( E_e \) is needed. Assuming that the elastic modulus is anisotropic but homogeneous, the microscopic elasticity theory of Khachaturyan [42] is often used in phase field simulations. For example, the elasticity effect is incorporated by expressing the elastic strain energy as a function of field variables (see the discussion in, for example, [37, 49, 58, 64, 74]), and an earlier work [20]). To be specific, the total energy is given by

\[
E_t = \int_{\Omega} \left( f(\eta) + \frac{1}{2} |M \nabla \eta|^2 \right) dx + E_e
\]

(2.4)

where \( E_e \) is the elastic energy defined as

\[
E_e = \int_{\Omega} edx;
\]

(2.5)
with the elastic energy density $e$ calculated from:

$$ e = \frac{1}{2} C_{ijkl} \varepsilon_{ij}^{el} \varepsilon_{kl}^{el} , $$

The summation convention is used here. For a cubic material with its three independent elastic constants $c_{11}$, $c_{12}$ and $c_{44}$ in the Voigt’s notation, the elastic energy density takes on the form [42]:

$$ e = \frac{1}{2} c_{11} ( (\varepsilon_{11}^{el})^2 + (\varepsilon_{22}^{el})^2 + (\varepsilon_{33}^{el})^2 ) + c_{12} (\varepsilon_{11}^{el} \varepsilon_{22}^{el} + \varepsilon_{11}^{el} \varepsilon_{33}^{el} + \varepsilon_{22}^{el} \varepsilon_{33}^{el} ) + 2 c_{44} ( (\varepsilon_{12}^{el})^2 + (\varepsilon_{13}^{el})^2 + (\varepsilon_{23}^{el})^2 ) . $$

Here the elastic strain $\varepsilon^{el}$ is the difference between the total strain $\varepsilon$ and stress-free strain $\varepsilon^*$ since stress-free strain does not contribute to the total elastic energy, i.e.:

$$ \varepsilon_{ij}^{el} = \varepsilon_{ij} - \varepsilon_{ij}^* , $$

where the stress-free strain is

$$ \varepsilon_{ij}^* = (\varepsilon_0)_{ij} (\eta - \eta_0) . $$

Here, $(\varepsilon_0)_{ij}$ is a constant tensor and $\eta_0$ is the average order parameter of the system. The total strain $\varepsilon_{ij}$ may be represented as the sum of homogeneous and heterogeneous strains:

$$ \varepsilon_{ij} = \bar{\varepsilon}_{ij} + \delta\varepsilon_{ij} , $$

The homogeneous strain is defined in such a way so that

$$ \int_{\Omega} \delta\varepsilon_{ij} d\mathbf{x} = 0 . $$

The heterogeneous strain is related to the local displacement field $\{v_k\}$ by the usual elasticity relation,

$$ \delta\varepsilon_{ij} = \frac{1}{2} \left( \frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right) . $$
It also satisfies the mechanical equilibrium condition given by the elasticity equation
\[ \frac{\partial \sigma_{ij}}{\partial x_j} = 0 \]
with the stress components \( \sigma_{ij} = c_{ijkl} \varepsilon_{kl} \).

The elasticity equation with periodic boundary conditions can be solved in the Fourier space which leads to a more explicit form of \( E_e \) (see the details in [42]). For the case of a simply connected coherent inclusion in an anisotropic solid with cubic symmetry, if the phase transformation involves only one type of crystal lattice, the elasticity energy contribution can be further simplified to
\[ E_e = \frac{1}{2} \int_{\Omega} d\mathbf{k} B(\mathbf{n}) |\hat{\eta}(\mathbf{k}) - \hat{\eta}_0(\mathbf{k})|^2. \] (2.6)

\( \hat{\eta}(\mathbf{k}) \) is the Fourier transform of \( \eta(\mathbf{x}) \). The integration in (6.6) is over the reciprocal space \( \hat{\Omega} \) of the reciprocal lattice vector \( \mathbf{k} \), \( \mathbf{n} = \mathbf{k}/|\mathbf{k}| = (n_1, n_2, n_3) \) is the normalized unit vector and in three dimensions, and the term \( B(\mathbf{n}) \) is given by
\[ B(\mathbf{n}) = 3(c_{11} + 2c_{12}) \epsilon_0^2 - \frac{(c_{11} + 2c_{12})^2 \epsilon_0^2 (1 + 2\zeta s(\mathbf{n}) + 3\zeta^2 n_1^2 n_2^2 n_3^2)}{c_{11} + \zeta(c_{11} + c_{12}) s(\mathbf{n}) + \zeta^2 (c_{11} + 2c_{12} + c_{44}) n_1^2 n_2^2 n_3^2} \] (2.7)
where we employ the Voigt’s notation, \( \epsilon_0 \) is the lattice mismatch between the nucleating new cubic phase and the parent cubic phase, \( \zeta = (c_{11} - c_{12} - 2c_{44})/c_{44} \) is the elastic anisotropic factor, and \( s(\mathbf{n}) = n_1^2 n_2^2 + n_1^2 n_3^2 + n_2^2 n_3^2 \). We set, in particular that \( \mathbf{n} = 0 \) if \( \mathbf{k} = 0 \).

Taking into account the long-range elastic interactions and surface energy anisotropy, the increase in the total free energy arising from the order parameter fluctuation in an initially homogeneous state with \( \eta_0 \) is given by
\[ \Delta E_{\text{total}}(\eta) = \int_{\Omega} \left( \delta f(\eta) + \frac{M_1}{2} \eta_x^2 + \frac{M_2}{2} \eta_y^2 \right) d\mathbf{x} + \beta E_e \] (2.8)
where \( \delta f(\eta) = f(\eta) - f(\eta_0) \) and \( E_e \) is given by (6.6). Rather than varying the magnitudes of lattice mismatch and elastic constants, a factor \( \beta \) is introduced to study the effect of relative elastic energy contribution to chemical driving force on
the critical nucleus morphology.

2.4 Saddle points

Since nucleation takes place by overcoming the minimum energy barrier, a critical nucleus is defined as the spatial order parameter fluctuation which has the minimum free energy increase among all fluctuations which lead to nucleation. Therefore, we may find the critical nucleus by computing the saddle points of the energy functional of the order parameter $\eta$, that has the highest energy in the minimum action path. This is consistent with the large derivation theory which states that the most probable path (that minimizes the action [45]) passes through the saddle point in the large time limit.

2.4.1 Existence

Let us first study some basic theories concerning the existence of saddle points. For simplicity, we consider the case of isotropic surface energy only, that is, we take $M_1 = M_2$. In this case, for the convenience of mathematical analysis, a different scaling is often introduced so that it is equivalent to consider the saddle points of the following functional:

$$E_\epsilon(\eta) = \int_\Omega \left[ \frac{\epsilon}{2} |\nabla \eta|^2 + \frac{1}{4\epsilon} (\eta^2 - 1)^2 - \frac{\lambda}{2} (3\eta - \eta^3) \right] dx$$

$$+ \frac{\beta}{2(2\pi)^d} \int_\hat{\Omega} d\mathbf{k} B(\mathbf{n}) |\hat{\eta}(\mathbf{k}) - \hat{\eta}_0(\mathbf{k})|^2 , \tag{2.9}$$

with $B(\mathbf{n})$ as given by (6.11). To be more precise, we consider the variation of the energy $E_\epsilon$ in the Hilbert space $H^1_p(\Omega)$ which is the standard $H^1$ Sobolev space of the periodic functions defined on $\Omega$.

For the parameter range of interest to us, we may assume that there are two positive constants $M_1$ and $M_2$ such that

$$0 \leq M_1 \leq B(\mathbf{n}) \leq 3(c_{11} + 2c_{12})\epsilon_0^2 = M_2$$

uniformly in the unit sphere.
In the literature, a popular approach to study the existence of saddle points within the framework of calculus of variation is given by the mountain pass theorem, which often relies on the so called minimax technique [60]. Another approach has been developed recently in [41] to relate a saddle point of $E_\epsilon$ with its $\Gamma$-limit functional. In all these works, a key condition for the applicability is the Palais-Smale compactness condition:

**Definition 1.** (PS condition). Given a Hilbert space $H$, and a $C^1$ functional $E : H \to \mathbb{R}$, a sequence $\{u_k\}_{k=1}^\infty$ in $H$ is said to be a Palais-Smale sequence if

$$
\lim_{k \to \infty} \|\delta E(u_k)\|_{H^{-1}} = 0, \quad \text{and} \quad \{E(u_k)\}_{k=1}^\infty \text{ is bounded.} \quad (2.10)
$$

The functional $F$ is said to satisfy the Palais-Smale condition if every Palais-Smale sequence is precompact in $H$.

Here $H^{-1}$ refers to the conventional dual space of $H$ [21] and $\delta E$ denotes the first variation of the energy $E$. We now state the result that verifies the PS condition for the functional $E_\epsilon$ given by (2.9).

**Proposition 1.** The functional $E_\epsilon = E_\epsilon(\eta)$ given by (2.9) satisfies the Palais-Smale condition in $H^1_p(\Omega)$.

**Proof.** We follow similar lines as in [41]. Suppose that $\{\eta_k\}$ is a sequence satisfying the conditions

$$
\sup_k E_\epsilon(\eta_k) < \infty, \quad \lim_{k \to 0} \|\delta E_\epsilon(\eta_k)\|_{H^{-1}} = 0.
$$

Here, in the weak sense, the first energy variation is given by

$$
\delta E_\epsilon(\eta) = -\epsilon \Delta \eta + \frac{1}{\epsilon} (\eta^3 - \eta) + \frac{3\lambda}{2} (\eta^2 - 1) + \frac{\beta}{(2\pi)^d} \int_{\hat{\Omega}} B(n)(\hat{\eta}(k) - \hat{\eta}_0(k)) e^{i k x} \, dk.
$$

By the energy bound, we get a uniform $H^1$ bound. Hence, there is a subsequence $\{k_j\}$ such that

$$
\eta_{k_j} \to \eta \text{ in } H^1_p(\Omega) \quad \text{and} \quad \eta_{k_j} \to \eta \text{ in } L^p(\Omega), \quad 1 \leq p < 2d/(d-2)
$$
for some $\eta \in H^1_p(\Omega)$. By the assumption on $B(n)$ and the Parseval identity, we easily see that

$$\lim_{j \to \infty} \int_{\Omega} d\kappa B(n)|\hat{\eta}_j(k) - \hat{\eta}_0(k)|^2 = \int_{\Omega} d\kappa B(n)|\hat{\eta}(k) - \hat{\eta}_0(k)|^2.$$

By the conditions

$$<\delta E_{\epsilon}(\eta_k), \eta_k> \to 0 \quad \text{and} \quad <\delta E_{\epsilon}(\eta_k), \eta > \to 0,$$

we then get

$$\lim_{j \to \infty} \int_{\Omega} |\nabla \eta_j|^2 d\Omega = \lim_{j \to \infty} \left\{ \int_{\Omega} g(\eta_j) d\Omega - \frac{\beta}{\epsilon(2\pi)^d} \int_{\Omega} d\kappa B(n)|\hat{\eta}_j(k) - \hat{\eta}_0(k)|^2 \right\}$$

$$= \int_{\Omega} g(\eta) d\Omega - \frac{\beta}{\epsilon(2\pi)^d} \int_{\Omega} d\kappa B(n)|\hat{\eta}(k) - \hat{\eta}_0(k)|^2$$

$$= \int_{\Omega} |\nabla \eta|^2 d\Omega$$

where $g = g(\eta)$ denotes

$$g(\eta) = \frac{1}{\epsilon^2}(\eta^4 - \eta^2) + \frac{3\lambda}{2\epsilon}(\eta^3 - \eta).$$

The norm convergence with the weak convergence together means that the sequence is convergent strongly in $H^1$, we thus have the PS condition satisfied. Q.E.D.

With the PS condition, one may apply the mountain pass type theorems to get the saddle point of the energy [60]. For a given constant positive driving force, it can be seen that when $\epsilon$ is suitably small, on the boundary of a small $H^1$ ball of the solution $\eta_0=-1$, the energy is strictly larger than $E_{\epsilon}(\eta_0)$, moreover, for small $\epsilon$, $E_{\epsilon}$ at $\eta = 1$ is strictly less than the energy $E_{\epsilon}(\eta_0)$. The mountain pass theorem can thus be applied [60] and there must be a saddle connecting the path between $\eta=\eta_0=-1$ and $\eta=1$ with the lowest energy barrier. Due to the periodic boundary condition, it is possible to have a constant solution as the saddle point. For small $\epsilon$, the energy of such a trivial saddle is of $O(\epsilon^{-1})$, but one may easily construct
a path (for instance via tanh profiles [16]) which would have an energy barrier of $O(1)$. Thus, a non-trial saddle point exists.

### 2.4.2 Γ-convergence

With the PS condition, one may also adopt similar techniques as that presented in [41] to connect the saddle point of $E_\epsilon$ with the saddle point of the $\Gamma$-limit as $\epsilon \to 0$. Let us briefly recall the concept of $\Gamma$-convergence which is defined through two requirements: given a Banach space $U$, a sequence of functionals, $E_\epsilon : U \to R$, $\Gamma$-converges to a limiting functional $E_0$ as $\epsilon \to 0$ if for every $u \in U$ one has

i) whenever $\{u_\epsilon\} \subset U$ converges to $u$, then $\liminf_{\epsilon \to 0} E_\epsilon(u_\epsilon) \geq E_0(u)$, and

ii) there exists a sequence $\{\tilde{u}_\epsilon\} \subset U$ such that $\tilde{u}_\epsilon$ converges to $u$ and

$$\lim_{\epsilon \to 0} E_\epsilon(\tilde{u}_\epsilon) = E_0(u).$$

The notion of $\Gamma$-convergence has proven to be a powerful tool to study the limit of minimizers of functional sequences $E_\epsilon : U \to R$ whose conventional limit is typically defined on another Banach space $V$ which has a weaker topology. For example, in [27], the $\Gamma$-convergence of the minimizers for a free energy of the form (2.4), which includes both the interfacial energy and the elastic misfit energy as that given in (2.5), has been studied. More recently, $\Gamma$-convergence was also used to study the unstable saddle points of Ginzburg-Landau like functionals in [41]. The latter naturally applies to the case we consider here. The limiting functional is given as follows: for any $v \in L^1(\Omega)$,

$$E_0(v) = \begin{cases} \frac{\sqrt{2}}{3} \int_\Omega |\nabla v| d\Omega + \int_\Omega \lambda v d\Omega & \text{if } v \in BV(\Omega, \{\pm 1\}), \\ + \frac{\beta}{2(2\pi)^d} \int_\Omega d\mathbf{k} B(\mathbf{n}) |\hat{v}(\mathbf{k})|^2 & \text{if } \int_\Omega d\mathbf{k} B(\mathbf{n}) |\hat{v}(\mathbf{k})|^2 \\ \infty & \text{otherwise}. \end{cases}$$  \quad (2.11)$$

If the zero level set of $v$ is rectifiable, then by the co-area formula, we may also use the perimeter of the zero level set of $v$ to replace the first integral in the functional. The second term is obviously the bulk energy (volume) difference,
and the third term is due to the elastic contribution. We thus have the problem of finding the critical point of the functional $E_0$ as the $\Gamma$-limit. This is also commonly referred to as the sharp interface limit of the phase field model. Note that the form given here does not require the explicit use of the displacement field and is simpler than the case considered in [27, 28].

The saddle point of $E_0$ can also be computed via direct geometric modeling of the zero level set of $v$, especially when a simply connected inclusion is of interest. A level set approach can also be developed similar to the case without the elastic energy. We however elect to work with the original phase field energy, both for its rich physical origin and for future coupling with the phase field simulation of the microstructure evolution [7].

### 2.5 Numerical approximation

#### 2.5.1 Euler-Lagrange equation

By the calculus of variation, the saddle points to be computed are the solutions of the Euler-Lagrange equation of $\Delta E_{\text{total}}$, or without loss of generality, that of $E_\epsilon$:

$$\epsilon \Delta \eta = \frac{\eta^3 - \eta}{\epsilon} + \frac{3\lambda}{2}(\eta^2 - 1) + \frac{\beta}{(2\pi)^d} \int_{\hat{\Omega}} B(n)(\hat{\eta}(k) - \hat{\eta}_0(k)) e^{ikx} dk,$$

in the domain $\Omega$, subject to the periodic boundary condition.

The above equation can be viewed as a nonlocal perturbation to some well studied semi-linear elliptic equation. Due to the periodic boundary condition, the non-locality can be efficiently treated in the Fourier space, thus a Fourier spectral approximation is appropriate.

#### 2.5.2 Fourier spectral method

For analysis of Fourier spectral approximations, we borrow the abstract framework developed in [4]. Taking for instance $\beta$ as a parameter, we may view the computed Fourier spectral solution as an approximation to an nonsingular branch of solutions of (4.28). We denote $\eta_N(\beta)$ as the spectral solution with $N$ Fourier modes in each variable directions. With given $\epsilon$, the phase field solutions are smooth (and ana-
lytic), and the nonlinear part as well as the part involving the elastic contributions can be seen as a smooth compact perturbation to the principal linear elliptic part, moreover, it is easy to see that except at certain critical values of $\beta$, each solution branch is smooth in $\beta$ and is isolated. We then have a general error estimates for the Fourier spectral approximation:

**Theorem 1.** Let $\Lambda$ be a compact interval in $\mathbb{R}$, and let $\eta = \eta(\beta)$ be a regular smooth solution branch of (4.28). Then, for $N$ sufficiently large, there exists a unique regular branch of $\eta_N = \eta_N(\beta)$ in a neighborhood of $\eta = \eta(\beta)$ which is the approximate Fourier spectral solution of (4.28) such that

$$\lim_{N \to \infty} \| \eta(\beta) - \eta_N(\beta) \|_{H^1_p(\Omega)} = 0.$$ 

Moreover, there exist positive constants $c$ and $\sigma$, independent of $N$ for $N$ large, such that

$$\| \eta(\beta) - \eta_N(\beta) \|_{H^1_p(\Omega)} \leq ce^{-\sigma N}. \quad (2.13)$$

The proof of the above theorem can be constructed by coupling standard error estimates for the linear elliptic equations with the general theory for nonlinear problems developed in [4] (for applications to Ginzburg-Landau and phase field type of models that are similar to ones considered here, one may also consult [15, 17]). We omit the details. The numerical results reported later confirm such accuracy. Naturally, in many practical situations, one may be interested in the dependence of the numerical accuracy with the model parameters such as the interfacial width parameter $\epsilon$. We refer to [22] for some studies on more precise estimates with respect to the parameters. Computationally, it is found that the spectral scheme performs well, even for very small $\epsilon$, in comparing with low order finite difference or finite element schemes, but a complete theoretical understanding is lacking at the moment.

### 2.5.3 Numerical Algorithm

In the actual computational implementation, we do not solve the Euler-Lagrange equation directly as the saddle point are unstable critical points of the energy. Instead, we use some sophisticated numerical schemes to assure robustness and
stability. There are various approaches for solving variational problems numerically. While the most notable ones are for finding minimizers, algorithms have also been developed to find minimum energy paths and to search for saddle points [18, 23, 34, 36, 40, 51]. Here, to find the saddle points, we employ an algorithm which adopts the minimax technique in the calculus of variation and optimization [57, 60]. A natural idea of the minimax algorithm is to first define a solution submanifold $\mathcal{M}$ such that a local minimum point of $\Delta E_{\text{total}}$ on $\mathcal{M}$ yields a saddle point on the full manifold. Thus the problem becomes a minimization of $\Delta E_{\text{total}}$ on the submanifold, and a saddle point becomes stable on the submanifold $\mathcal{M}$. Here, to ensure stability and monotonicity, a steepest descent search is applied to approximate a local minimizer of $\Delta E_{\text{total}}$ on submanifold $\mathcal{M}$. Meanwhile, it is imperative that a return rule is used to prevent the descent search from leaving the submanifold so as to guarantee the convergence of the algorithm.

We follow the approach studied by Li and Zhou [51] which is outlined below:

1. For $k = 0$, take a direction $\nu_0$ at a local minimum $\eta_0$, define

   $\mathcal{M}_0 = \{\eta_0 + \text{span}\{\nu_0\}\}$

   and search for a local maximum in $\mathcal{M}_0$, i.e., solve

   \[
   w^k = p(\nu_0) := \arg\max_{u \in \mathcal{M}_0} \Delta E_{\text{total}}(u).
   \]

2. For $k \geq 0$, compute the variational gradient $g^k$ of $\Delta E_{\text{total}}$ at $w^k$. If $\|g^k\|$ is less than some tolerance, stop and output $w^k$ as a critical nucleus, else goto Step 3.

3. Given a step-size parameter $\hat{b}_k$, let

   $\mathcal{M}_b^{k+1} = \{\nu_k + \text{span}\{\nu_b^k\}\}$

   with $\nu_b^k$ being the unit vector in the direction of $\nu^k - bg^k$ and $b$ in $(0, \hat{b}_k)$, let

   \[
   p(\nu_b^k) := \arg\max_{u \in \mathcal{M}_b^{k+1}} \Delta E_{\text{total}}(u) .
   \]
Solve

\[ b^* := \arg \min_{0 < b < b_k} \Delta E_{total}(p(\nu_b^k)) \],

set \( \nu^{k+1} = \nu_b^k \), \( w^{k+1} = p(\nu^{k+1}) \), update \( k \) by \( k + 1 \) and go to step 2.

We refer to [51] for additional discussions and the convergence properties of the above algorithm.

For computational efficiency, we find that it works well to choose a \( \tanh \) profile as the initial search direction in the first step. The argument of the \( \tanh \) function is a scaled distance to some prescribed level set. In Step 2, the number \( \hat{b}_k \) is used to control the step-size of the steepest descent search. This is important for the stability of the algorithm. Again, in each of the steps, the Fourier spectral methods are used to solve the resulting PDEs or to compute the energy variations, which allows very efficient computation via FFT. In addition, we note that an inner product given by the integral of the product of the functions and their gradients is adopted in Step 2 to define the variational gradient \( g^k \) which is computed again via FFT in the Fourier spectral discretization. This technique is similar to the use of a spectrally equivalent preconditioner for the Hessian matrix in the numerical solution of minimization problems.

### 2.6 Numerical examples

We now present illustrative numerical examples that demonstrate the convergence of the numerical scheme and examples that offer some hints on the critical nucleus morphologies in cubically anisotropic systems. We take the energy scaled in the form (2.9) with \( \eta_0 = -1 \), \( c_{11} = 250 \), \( c_{12} = 150 \), \( c_{44} = 100 \) in all of our simulations. The other parameters may change for different cases and they are specified later.

First, we conduct a series of numerical experiments in two dimensions to verify the spectral accuracy of the computed solution. Since for most of the physically relevant cases, there is no exact analytic solution available, we simply compare other numerical solutions with that computed with the most number of Fourier modes (with the highest level of numerical resolution). The comparison is done in two fronts, one with a fixed interfacial width \( \epsilon = 1/32 \), while the number of Fourier modes changes from \( 64^2 \) to \( 128^2 \), \( 256^2 \) and finally \( 512^2 \). Here, we take \( \lambda = 6 \) and
\[ \beta = 0.3 \text{ and } \epsilon_0 = 0.1. \]

The plots of the computed solutions are given respectively in Figure 6.7, corresponding to different grids. The non-convex shape of the critical nuclei is a signature property due to the anisotropic elastic energy contribution \cite{75}. In Figure 2.3, the logarithms of the \( H^1 \) error norms (measuring both the error in the function and its first order spatial derivatives) are plotted for the numerical solutions computed with different number of Fourier modes. The stars and circles are data points for the computed logarithms of the \( H^1 \) error. The solid and dash lines are their respective least square fits using linear polynomials. It can be seen that the errors are reduced exponentially when the nodes are doubled in each direction, thus it illustrates the spectral accuracy of the numerical solutions.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2_2.png}
\caption{Plots of critical nuclei for \( \epsilon=1/32 \)}
\end{figure}

We also compute the solutions with a gradually decreasing \( \epsilon \), that is, we take \( \epsilon=2/N \) where \( N \) is the number of Fourier modes used in each direction. The plots of the computed solutions are given in Figure 2.4. We have found that adequate resolutions are maintained for all values of \( \epsilon \), and, as expected, the interfacial layers
are getting sharper for smaller $\epsilon$ while the shapes remain nearly identical. Since the sharp interface limit is no longer in $H^1$, we measure the $L^2$ difference in the norms instead, and the results are given as errors in Table 1 also, which show that as $\epsilon$ goes to zero, the solution is convergent to a sharp interface solution.

<table>
<thead>
<tr>
<th>Fourier modes</th>
<th>$N = 64$</th>
<th>$N = 128$</th>
<th>$N = 256$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Errors</td>
<td>1.0509e-002</td>
<td>2.8876e-003</td>
<td>5.3744e-004</td>
</tr>
</tbody>
</table>

Table 2.1. Errors of Fourier spectral solutions for changing $\epsilon$.

### 2.7 Conclusion

Our recent works demonstrate that the morphology of a critical nucleus, or a critical fluctuation in elastically anisotropic solids can be predicted by a combination of the diffuse-interface approach and the minimax algorithm. The nucleation profile calculation is shown to be mathematically well-posed with the diffuse-interface energy under consideration. Its relation to sharp interface models is also revealed.
Although there have been extensive theoretical studies of particle morphologies during growth or coarsening by minimizing the total interfacial and elastic strain energy [13, 28, 50, 70], our method provides a new approach to predict the morphologies of saddle-point critical nuclei without any \textit{a priori} assumptions on the shapes. The Fourier spectral discretization works efficiently in the implementation of the minimax algorithm and provides an efficient and robust procedure for the critical nuclei calculation. The calculations reveal the fascinating possibility of nuclei with non-convex shapes and the formation of critical nuclei whose symmetry is lower than both the new phase and the original parent matrix. It should be noted that the present work ignores the possible presence of defects such as dislocations and interfaces, i.e. heterogeneous nucleation. We are presently studying generalizations to such cases as well as the effective coupling of the critical profile calculation with the phase field simulation of microstructure evolutions.
Simulation of critical nucleus morphology in solid-state phase transformations

3.1 Introduction

Nucleation happens when a material becomes thermodynamically meta-stable with respect to its transformation to a new state or new crystal structure. Some common nucleation phenomena include formation of liquid droplets in a saturated vapor, appearance of ordered domains in a disordered solid, or nucleation of tetragonal variants in a cubic matrix, etc. Very often, it is the nucleation process that dictates the microstructure of a material.

Much of our current understanding of nucleation owes to the classical nucleation theories developed 1930s. Early nucleation theories mostly considered phase changes in fluids, e.g. a liquid droplet in a vapor phase, and it is natural that they assumed spherical shapes for the critical nuclei. The thermodynamic properties of a nucleus are assumed to be the same as in the corresponding bulk. The size of a critical nucleus is then determined as a result of bulk free energy reduction and interfacial energy increase, $r = -2\gamma/\Delta G_\nu$ where $\gamma$ is the interfacial energy per unit area between a nucleus and the parent matrix and $\Delta G_\nu$ is the free energy driving force per unit volume. Despite the assumptions of spherical shapes for critical
nuclei, the same classical theories have been utilized to interpret kinetics of many phase transformations involving solids including solid to solid transformations. As a matter of fact, for some systems, the classical nucleation theory has been shown to provide a good description on the nucleation kinetics.

While it is reasonable to assume spherical shapes for nuclei during fluid-fluid phase transitions, the morphology of critical nuclei in solids is expected to be strongly influenced by anisotropic interfacial energy and anisotropic elastic interactions. For example, nuclei for $\gamma'$ precipitates in Ni-alloys can be cuboidal or spherical depending the lattice mismatch between the precipitate and matrix, $\theta'$ precipitates in Al-Cu are plates, and the $\beta'$ precipitates in Al-Mg-Si alloys are needle-shaped. The morphology of a critical nucleus in the presence of interfacial energy anisotropy alone can be deduced from the well-known Wulff construction. However, predicting the shape of a critical nucleus in the presence of both elastic energy and surface energy anisotropy is particularly challenging since elastic energy contribution depends on the morphology of a nucleus and lattice mismatch between the nucleus and the matrix. As a result, prior applications of the classical nucleation theory to solid state transformations typically make assumptions on the shape of a nucleus as an $a$ priori, and the elastic energy contribution to nucleation is included as an extra barrier for nucleation, which is proportional to volume, i.e., $a^* \sim -\beta^* \gamma/(\Delta f_\nu + E_{el})$ where $a^*$ represents the critical size of a nucleus, $\Delta f_\nu$ is the bulk driving force for nucleation, $\beta^*$ is a numerical factor depending on the shape of the nucleus, and $E_{el}$ is the elastic strain energy contribution to nucleation on the order of $C\epsilon_0^2$ where $C$ is the elastic modulus and $\epsilon_0$ is the lattice mismatch strain (transformation strain, eigenstrain, stress-free strain) between the nucleus and the matrix.

Another theoretical approach to nucleation is based on the diffuse-interface description, also called the non-classical nucleation theory. In this approach, the properties within a nucleus are inhomogeneous and the interface between the nucleus and parent matrix is diffuse. Following the seminal work of Cahn and Hilliard [6], the diffuse-interface approach has been previously applied to nucleation in solids. For example, Roitburd et al [62] and Khachaturyan et al [42, 44] described the nucleation of a new phase in solid solutions and the general problem of extreme states of solid solutions using the diffuse interface model. Later on, Roy et al [63]
discussed the nucleation in the presence of a general long-range interaction. The focus is on the critical order parameter profiles rather than predicting the morphology of a nucleus. Wang and Khachaturyan [72] examined the morphology of nuclei during a martensitic transformation by switching on and off Langevin noise. The particles obtained using this approach do not necessarily correspond to saddle point configurations associated with a critical nucleus. Poduri and Chen [59] studied the nucleation of an ordered precipitate from a disordered matrix by extending the diffuse-interface theory of Cahn and Hilliard. Roitburd [61] and Chu et al [10] were the first to explore the nucleation of martensites using the non-classical approach. More recently, Gagne et al [26] studied the morphological evolution using Langevin simulations of martensitic transformations in two dimensions. They concluded that systems with long-range interactions quenched into a meta-stable state near the pseudo-spinodal exhibit nucleation that is qualitatively different from classical nucleation near the coexistence curve. It is noted that all existing diffuse interface theories for nucleation in solids ignore the anisotropic interfacial energy and anisotropic long-range elastic interactions. Within the phase-field approach, nucleation during solidification has been studied by Granasy et al [30, 31], and nucleation in solids in the presence of elastic interactions by Hu and Chen [37], Zhang et al [82], Shen et al [66], and Luo et al [54]. Using a microscopic model, LeGoues et al [48] studied the influence of crystallography upon critical nucleus shapes and kinetics of homogeneous nucleation by combining the discrete lattice mean-field model with the microscopic theory of strain energy. They considered both the influence of anisotropic interfacial energy and anisotropic strain energy on nucleation. However, they also assumed that the shapes of the critical nuclei were either spherical or plates.

In recent works [75, 76, 77], we propose a computational approach for predicting the morphology of a critical nucleus as an extreme state in two dimensions by considering the presence of both interfacial energy anisotropy and elastic interactions [75]. Some rigorous mathematical and numerical analysis of the underlying framework are discussed in [77]. In [76], we extend the model and the numerical implementation to three dimensions and discuss the influence of elastic energy on the morphology of critical nucleus and shape bifurcations as strain energy contribution increases. The key elements of our approach involve the diffuse-interface
description of the nucleation problem [6] and the minimax algorithm in the calculus of variation [60]. It should be emphasized that the problem under consideration is spatially inhomogeneous and it is different from the saddle point search when a solid is homogeneously transformed to a near phase throughout the system, described by a homogeneous free energy as a function of a homogeneous order parameter.

In this Chapter, we implement a diffuse interface model combined with the minimax technique to predict the morphology of critical nuclei during solid to solid phase transformations in both two and three dimensions. It takes into account the anisotropic interfacial energy as well as the anisotropic long-range elastic interactions. It is demonstrated that the morphology of critical nuclei in cubically anisotropic solids can be efficiently predicted by the computational model without a priori assumptions. A particular example of cubic to cubic transformation within the homogeneous modulus approximation is considered. It is shown that strong elastic energy interactions may lead to critical nuclei with a wide variety of shapes including plates, needles, and cuboids with non-convex interfaces. To offer additional understanding on the competition of interfacial and elastic energies, we also examine the various energy contributions analytically in a sharp interface limit.

3.2 Diffuse Interface Model

Following [75], we consider the case of a structural transition with no compositional changes. It is further assumed that the structural difference between the parent phase and the nucleating phase can be sufficiently described by a single order parameter $\eta$. Extensions to more general cases, e.g., nucleation of a new phase in a solid solution, can also be considered in a similar fashion, and will be pursued in subsequent works.

For a given temperature, a double-well potential is chosen to describe the free energy dependence on $\eta$: $f(\eta) = (\eta^2 - 1)^2/4 - \lambda h(\eta)$. The two local energy wells are at $\eta = \pm 1$ and $h(\eta) = (3\eta - \eta^3)/2$ respectively so that $2\lambda$ gives the bulk driving force for the phase transformation from the $\eta = -1$ state to the $\eta = +1$ state (as illustrated in Fig.3.3).

The total free energy of an inhomogeneous system described by a spatial dis-
Figure 3.1. Double well potential

tribution of $\eta$ could be written as:

$$E = \int_\Omega \left( f(\eta) + \frac{\alpha}{2} |\nabla \eta|^2 \right) dx .$$

where $\alpha$ is the gradient energy coefficient in $\Omega$ for the isotropic interfacial energy, and the domain $\Omega = (-1, 1)^d$ is used with $d = 2$ or $3$ being the space dimension and a periodic boundary condition is used for the order parameter $\eta$.

In the case that the interfacial energy is anisotropic, as is usually the case for nucleation in solids, either the gradient energy coefficient can be expressed as a second or higher order derivatives, or rather artificially but common in the phase-field models, it is made directionally dependent. To incorporate the effect of long-range elastic interactions on the morphology of a critical nucleus, and thus the nucleation barrier, the computation of the elastic energy is needed for any arbitrary distribution of $\eta$. We hereby assume that the elastic modulus is anisotropic but homogeneous so we may employ the microscopic elasticity theory of Khachaturyan [42]. For a cubic crystal, we have

$$E_{\text{elastic}} = \frac{1}{2} \int_{\Omega} \frac{dk}{(2\pi)^d} B(n)|\hat{n}(k)|^2$$

(3.1)

which is over the whole reciprocal space $\hat{\Omega}$. The reciprocal lattice vector, $k$, is given in Chapter 2.

Incorporating the long-range elastic interactions and a simple form of the surface energy anisotropy, the total free energy increase arising from the order parameter fluctuation in an initially homogeneous state with $\eta_0$ is given by

$$\Delta E_{\text{total}} = \int_{\Omega} \left( \delta f(\eta) + \frac{\alpha_x}{2} \eta_x^2 + \frac{\alpha_y}{2} \eta_y^2 \right) dx$$
\[ + \frac{\beta}{2(2\pi)^d} \int_{\Omega} d\mathbf{k} B(\mathbf{n}) |\hat{\eta}(\mathbf{k}) - \hat{\eta}_0(\mathbf{k})|^2, \quad (3.2) \]

where \( \delta f(\eta) = f(\eta) - f(\eta_0) \). Instead of changing the magnitudes of lattice mismatch and elastic constants, a factor \( \beta \) is introduced which effectively characterizes the relative elastic energy contribution to the free energy driving force in determining the critical nucleus morphology.

### 3.3 Numerical Algorithm

As nucleation can be achieved by overcoming the minimum energy barrier, a critical nucleus may be defined as the spatial order parameter fluctuation which allows the minimum free energy increase among all fluctuations which lead to nucleation. Such a scenario is consistent with the large derivation theory which states that the most probable path (that minimizes the action [45]) passes through the saddle point in the large time limit. In the study here, our primary interest is to examine the effect of elastic energy contributions on the critical nucleus profiles, which can be found by computing the saddle point of the energy functional, of the order parameter \( \eta \), that has the highest energy along the minimum action path.

By the usual calculus of variation, a saddle point is necessarily a solution of the Euler-Lagrange equation corresponding to the energy \( \Delta E_{\text{total}} \):

\[
\alpha_x \frac{\partial^2 \eta}{\partial x^2} + \alpha_y \frac{\partial^2 \eta}{\partial y^2} = \frac{\partial}{\partial \eta} \delta f(\eta) + \frac{\beta}{(2\pi)^d} \int_{\Omega} B(\mathbf{n})(\hat{\eta}(\mathbf{k}) - \hat{\eta}_0(\mathbf{k})) e^{i\mathbf{k}\cdot\mathbf{x}} d\mathbf{k}, \quad (3.3)
\]

subject to the periodic boundary condition. The equation (6.5) can be viewed as a nonlocal perturbation, due to the elastic contribution, to some well studied semilinear elliptic equation [60]. We recall that there have been various approaches proposed for solving variational problems numerically which include, in particular, methods for the computation of saddle points and minimum energy paths [23, 34, 36, 40, 51]. While a couple of different approaches have been successfully implemented for the problem under consideration, the results reported here are based on the use of the minimax technique that has been studied extensively in calculus of variation and optimization [57, 60]. Similar computational results have also been obtained via other approaches, further validating the computational
findings presented in the later examples.

In less technical terms, the main idea of the minimax algorithm is to first define a solution submanifold $\mathcal{M}$ such that a local minimum point of $\Delta E_{\text{total}}$ on $\mathcal{M}$ yields a saddle point of the energy. Thus, the saddle point computation is effectively transformed into a minimization of $\Delta E_{\text{total}}$ on the submanifold, and a saddle point becomes stable on the submanifold $\mathcal{M}$. The detailed numerical algorithm is given in Chapter 2. Earlier applications of the minimax algorithm often focus on well known semi-linear elliptic equations in the calculus of variation. We hereby give some comments on the implementation of the algorithm. First, with the periodic boundary condition, the non-locality due to the elastic contributions can be efficiently treated in the Fourier space, thus a Fourier spectral method becomes appropriate when the minimax algorithms are implemented in the numerical computation [8, 75]. Secondly, to enhance the computational efficiency, we find that it works well to choose a $\tanh$ profile as the initial search direction in the first step. The argument of such a $\tanh$ function is a scaled distance to some prescribed level set. Thirdly, in Step 2, the number $\hat{b}_k$ is used to control the step-size of the steepest descent search, which is important for the stability of the algorithm.

Furthermore, the Fourier spectral method has been proven to be highly accurate and efficient. More theoretical analysis and numerical tests of the discretization can be found in [75]. Moreover, in the second step, in order to accelerate the convergence, we adopt the so-called $H^1$ inner product for the definition of the variational gradient $g^k$. Such an inner product of any two functions is given by the integral of the sum of their product and the product of their gradients. This effectively defines the variational gradient of the energy functional in the so-called $H^{-1}$ sense which is a dual space of $H^1$ and is often used in energy minimizations [69]. In our case, the computation of the variational gradient is particularly convenient as it can be computed again via FFT in the Fourier spectral discretization.

In addition, we also note that, depending on the choice of the initial profiles, several different saddle points may be found. As often the case for solving non-linear equations, we take a parameter continuation approach (with respect to the parameter $\beta$, in particular) to compute the various solution branches for the saddle points. The critical nuclei may be identified, for a particular parameter value, by comparing the energy of the saddle points on the different branches. While it
may not be possible to exhaustively search for all possible saddle points, efforts are made on using many different initial profiles to ensure those with lower energy values are successfully found in the numerical computation.

3.4 2D critical nucleus morphology in solid state transformations

A number of computer simulations are carried out in order to make predictions on the critical nucleus morphologies based on the developed model and the numerical algorithm. Here, results of both two-dimensional and three-dimensional simulations are reported for the particular example of cubic to cubic transformation within the homogeneous modulus approximation.

We now present illustrative numerical examples that demonstrate the convergence of the numerical scheme and examples that offer some hints on the critical nucleus morphologies in cubically anisotropic systems. We take the energy scaled in the form (2.9) with \( \eta_0 = -1, c_{11} = 250, c_{12} = 150, c_{44} = 100 \) in all of our simulations. The other parameters may change for different cases and they are specified later.

3.4.1 Anisotropic interfacial energy

We first consider the case of interfacial energy anisotropy where the gradient energy coefficient is dependent on directions. We take \( \beta = 0 \) in the equation (3.2). Fig.3.3 shows critical order parameter profiles without \( (\alpha_y/\alpha_x = 1 \) for left-most picture) and with interfacial energy anisotropy \( (\alpha_y/\alpha_x = 3, \) the second picture from the left). The predicted profile in the anisotropic case correctly displays the ellipsoidal direction-dependence as one would expect from the interfacial energy anisotropy. Note that although for a given interfacial energy anisotropy, the shape can be determined from the Wulff construction, the proposed diffuse-interface approach is able to predict both the size and shape of a critical nucleus simultaneously.
Figure 3.2. Critical nuclei with $\alpha_y/\alpha_x = 1, 3$ and $\beta = 0$, and nuclei in the cubically anisotropic system with $\beta = 0.2, 0.8, 1.2$ and $\alpha_y/\alpha_x = 1$.

### 3.4.2 Anisotropic elastic energy contribution

Examples of predicted critical profiles in the presence of long-range elastic interactions are shown in Fig.3.3 (from center to the right). We let $\eta_0=1, \alpha_x = \alpha_y = 4 \times 10^{-4}, \lambda = 0.05$ and assume $c_{11}=250, c_{12}=150, c_{44}=100, \epsilon_0 = 0.01$. We plot the critical order parameter profiles for $\beta = 0.2, 0.8$, and 1.2 respectively.

Figure 3.3. Critical nuclei with $\alpha_y/\alpha_x = 1, 3$ and $\beta = 0$, and nuclei in the cubically anisotropic system with $\beta = 0.2, 0.8, 1.2$ and $\alpha_y/\alpha_x = 1$.

As shown in Fig.3.3, long-range elastic interactions can dramatically change the critical nucleus morphology. A strong elastic interaction may lead to critical nuclei with cuboidal, or plate-like, or even the possibility of non-convex shapes (see Fig.3.3 for $\beta = 0.8$). One may find, in other studies [13], shapes resembling those given here via a variety of similar models. Although there have been extensive theoretical studies of elastic energy on the morphologies of an equilibrium particle by minimizing the total interfacial and elastic strain energy, the present work provides a new approach to predict the morphologies of critical nuclei without any a priori assumptions on the shapes.
3.4.3 Critical nucleus with diffuse interface

To see the effect of the diffuse interfacial width, in Fig.3.4, we take $c_{11}=250$, $c_{12}=c_{44}=50$, and plot respectively the critical nucleus profiles computed with different values of interfacial width corresponding to 0.06, 0.1 to 0.15. It can be seen that the interfaces diffuse more with larger interfacial width. Due to the elastic interactions, the shapes of the critical nuclei are also no longer completely circular.

![Figure 3.4](image)

Figure 3.4. Critical nuclei with diffuse interface width 0.06, 0.1 and 0.15.

3.4.4 2D most probable nucleus morphology

To determine the most probable nucleus morphology for a given relative elastic energy and chemical driving force contributions, we plot in Fig.3.5 the formation energy of a critical nucleus for different $\beta$ with the same $\epsilon_0$, $\lambda$, $\alpha$ as in Fig.3.3 and $c_{11}=250$, $c_{12}=150$, $c_{44}=200$. Here, the inserts contain the contour plots of a number of nucleus profiles as $\beta$ changes, illustrating the change in the critical nucleation morphology; the small squares and circles are data points based on the computed critical order parameter profiles, and the solid curves are least square fits by cubic polynomials. For small $\beta$, the critical nucleus with lower energy possesses the symmetry of a cubic crystal, i.e. either nearly-circular or square with rounded corners. As $\beta$ increases to be above 0.35, the nucleus becomes non-convex. For even larger $\beta$ (above 0.5), while one saddle point curve maintains the cubic symmetry, there is a second curve of saddle points with lower energy values corresponding to nuclei having lower symmetry groups. Continuing the latter curve for smaller $\beta$ below the intersection point shows that it leads to saddle points of higher energy than that for the non-convex, square and near circular nuclei.
Figure 3.5. Critical nucleation energy with changing elastic energy contribution and critical nuclei profiles.

3.4.5 More discussions and validations

Thus, we observe that stronger elastic energy contribution, the formation energy for a critical nucleus with a lower symmetry is lower than that with the cubic symmetry but non-convex interfaces (which are verified computationally to be indeed saddle point, with a 2d illustration of the local energy surface around the non-convex nucleus given in Fig.3.6 where one axis is along the solution direction, and another along a descent direction). To offer additional understanding on the competition of the elastic and interfacial energies, we compare the energies in Fig.3.6 for a nucleus in the shape of rectangle box of dimension $a$ by $1/a$ with a changing aspect ratio. Taking a sharp interface limit of our diffuse model, i.e., letting $\eta$ be a Heaviside function with $\pm 1$ inside and outside the box and substituting its Fourier coefficients $\{\hat{\eta}(k) = \sin(\pi k_x a) \sin(\pi k_y/a)/\left(\pi^2 k_x k_y\right)\}$ into (6.6), we get an estimation of the elastic energy (red solid curve), while the sharp surface energy is proportional to $2(a + 1/a)$ (blue dash curve). It is clear that while the surface energy is the smallest for $a = 1$ (thus preferring the cubic symmetry), the elastic energy is lower with lower symmetry. The diffuse interface model captures the competition and correctly distinguishes the ranges of parameters where one type of energy is dominant than the other. Thus, the nucleation of particles with a lower symmetry is dominant for large elastic energy contributions. It should be noted
that even in the two dimensional case, there are two equivalent variants form the
critical nucleus with a lower symmetry (the number of equivalent variants is then
three in three space dimension).

In our calculation, we also observe, as expected that, for a fixed $\beta$, with the
increase of the driving force, the size of critical nuclei reduces and the critical free
energy decreases, similar to that predicted from the classical nucleation theory for
spherical particles.

\[\text{Figure 3.6. Local energy surface near non-convex nucleus and a comparison of energies}
\text{for rectangular nuclei.}\]

### 3.5 3D critical nucleus morphology in solid state
transformations

#### 3.5.1 Anisotropic elastic energy contribution

We present some simulations of the three dimensional critical nuclei and examine
the effect of relative elastic energy contribution. The simulation results were ob-
tained on a $64^3$ three-dimensional computational grid. The Figures 3.7 and 3.8
contain computed isosurface plots of saddle point profiles corresponding to differ-
ent elastic energy contributions. In Fig.3.7 and 3.8, we take $c_{11}=250$, $c_{12}=150$,
$c_{44}=100$, $c_0 = 0.01$, $\eta_0 = -1$, $\alpha_x = \alpha_y = 9.7656 \times 10^{-4}$ and $\lambda = 0.3125$. Here we
should choose $\lambda$ big enough to avoid making the size of the critical nucleus too
large to fit in the domain $\Omega$.
Figure 3.7. 3D saddle point profiles for $\beta = 0, 0.63, 1.25$

Figure 3.8. 3D saddle point profiles in plate and needle shapes for $\beta = 0.31, 0.94, 1.56$

Similar to the previous findings based on the two dimensional computational results, the critical nuclei could be cuboidal, plate-like, and non-convex shapes. In addition, we find that the long-range elastic interaction may also lead to critical nuclei with needle shapes.

3.5.2 3D most probable nucleus morphology

To describe the 3D most probable nucleus morphology for a given relative elastic energy and given chemical driving force contributions, we plot in Fig.3.9(right) the formation energy of the saddle point profiles for different values of $\beta$ with the same parameters as in Fig.3.8. The circles, triangles and diamonds are data points based on the computed critical order parameter profiles, while the solid and dash curves are the least square fits of these data points by cubic polynomials. For small $\beta$, the critical nuclei with lower energy possess the symmetry of a cubic
crystal, i.e., they are either nearly spherical or take on shapes like a cube with rounded corners. As $\beta$ increases to be above 0.94, the nucleus becomes non-convex. For even larger $\beta$ (above 1.4), while one saddle point curve maintains the cubic symmetry, there is a second curve of saddle points with lower energy values corresponding to nuclei having lower symmetry groups. Continuing the latter curve for smaller $\beta$ below the intersection point shows that it leads to saddle points of higher energy than that for the non-convex, cube-like, and nearly circular nuclei. For some intermediate values of $\beta$, we again confirm, through our three dimensional simulation, the surprising result of critical nuclei with non-convex surfaces being the most probable morphology as previously observed in two dimensions [75]. It should be noted that this conclusion is reached by ignoring the possible presence of defects such as dislocations and interfaces, i.e., heterogeneous nucleation.

Next, Fig.3.9(left) plots critical free energy of formation as a function of bulk chemical driving forces $\lambda$ at fixed $\beta = 1.25$. The blue circles represent the data points for nonconvex-shape critical nuclei, and the red dash curve is least square fit by the exponential function. As expected, with the increase of the driving force, the size of critical nuclei (of cubic symmetry) is reduced and the critical free energy decreases. This dependence is similar to that predicted from the classical nucleation theory for spherical particles.

Figure 3.9. Critical nucleation energy with changing driving force (left) and changing elastic energy contribution (right).
3.5.3 Competition between the interfacial and elastic energies in the sharp interface limit

The profiles computed are verified to be indeed saddle points as discussed in [75]. Thus, we observe that, with a stronger elastic energy contribution, the formation energy for a critical nucleus with a lower symmetry is lower than that with cubic symmetry but with nonconvex interfaces. Meanwhile, we notice that, in the example computed here, the critical nucleation energy of the needle-shape nucleus is always higher than that of plate-shape nuclei corresponding to the same parameters. To gain better understanding on the competition of the elastic and interfacial energies, we consider the three dimensional analog of the discussions for the two dimensional case given in [75], and compare the energies in Fig.3.10 for cuboid nuclei of dimension $a$, $b$ and $1/(ab)$ with changing aspect ratios. To make the calculation analytically tractable, we carry out the calculation of the various energies, albeit in the sharp interface limit of the diffuse interface model. That is, we let $\eta$ be a Heaviside function with $\pm 1$ inside and outside the cuboid with its Fourier coefficients given by

$$\hat{\eta}(k) = \frac{\sin(\pi k_x a) \sin(\pi k_y b) \sin(\pi k_z/ (ab))}{\pi^3 k_x k_y k_z}.$$ 

Substituting it into (3.2), we can get an estimation of the elastic energy in Fig.3.10 (right). The sharp surface energy, meanwhile, is proportional to $2(ab + 1/a + 1/b)$ in Fig.3.10(left). These calculations indicate how the different energies are affected by the aspect ratio in the sharp interface limit and we may expect similar effects remain in the diffuse interface formulation. It is clear that the surface energy is the smallest for $a = b = 1$ (thus preferring the cubic symmetry), while the elastic energy is lower with high aspect ratios corresponding to either plate or needle shapes.

The three dimensional geometry leads to two possible configurations with lower symmetry. To see which lower symmetry is more probable, we further examine the surface energy and the elastic energy for some artificially constructed plate-like and needle-like shapes. We take the cuboid nuclei of dimension $a$, $a$ and $1/a^2$ and consider local minimizers over this special class of possible shapes, with $a > 1$.
being close to a plate-like shape while $a < 1$ resembling to a needle-like shape. We calculate the surface and elastic energies and choose a linear combination of two energies via a factor $\theta$ as the total energy $E_{\text{total}} = E_{\text{surface}} + \theta \cdot E_{\text{el}}$. In Fig. 3.11, the surface & elastic energies and the total energy are plotted with different $\theta$. We notice that, as $\theta$ is small, the total energy has a minimizer around $a = 1$, so the cubic symmetry is preferred. As $\theta$ increases to above 1, the total energy has two local minimizers at $a < 1$ and $a > 1$. The minimum energy at $a > 1$ is lower than that at $a < 1$, which means the plate-shape nuclei are more probable than the needle-shape nuclei. Although this calculation is for the sharp interface approximation of the a priori given shapes, it does offer a hint on the relation between needle shapes and plate shapes due to the competition between the interfacial and elastic energies. The diffuse-interface model captures this competition and effectively distinguishes the parameter ranges where one energy dominates the other, so that critical nuclei with the particular lower symmetry are identified as the most probable profiles for larger elastic energy contributions.

3.6 Conclusion

In this Chapter, a recently proposed diffuse interface approach for the study of critical nuclei morphologies in elastically anisotropic solids is discussed. The model and numerical implementation are extended to the three dimensional cases and
Figure 3.11. Surface and elastic energies and their various combinations. 

the influence of elastic energy on the morphology of critical nucleus and shape bifurcations is demonstrated as the strain energy contribution increases. Expanded discussions are provided on the background, models and algorithms, numerical convergence tests and numerical examples, along with sharp interface comparisons of the various energy contributions. Through the diffuse interface calculations, some fascinating observations are illustrated in three dimension on the presence of nuclei with non-convex shapes, and the formation of critical nuclei whose symmetry is lower than both the new phase and the original parent matrix. Additional insights into these numerically observed phenomena are offered via some simple analytical calculations in the sharp interface limit. Although there have been extensive theoretical studies of particle morphologies during growth or coarsening by minimizing the total interfacial and elastic strain energy [13, 28, 50, 70], our
method provides a new approach for the prediction of the morphologies of saddle-point critical nuclei without any *a priori* assumptions on the shapes. This approach can also be applied to nucleation of new phase particles in solid solutions, non-cubic systems, as well as to systems with defects such as dislocations and interfaces, i.e. heterogeneous nucleation.
4.1 Introduction

The problems of finding the saddle point have been a popular topic of great interest in many areas for a long time. A large spectrum of phenomena include conformational changes in macromolecules, chemical reactions to diffusion in condensed-matter systems and nucleation events during phase transformations [75].

It is well known that it is very difficult to compute the saddle points. First of all, the energy landscape is often complex in the high dimensional space. Second, the saddle point is not stable, so finding saddle points is much more challenging than finding energy minima. A large variety of ideas have already been proposed, for instance, the Minimax method [60], the Dimer method [34], etc. One particularly interesting approach is to search for the most probable transition path, or simply called the Minimum Energy Path (MEP), between the local minima of the total energy. The relevant saddle points can be identified with the highest energy point on the MEP. Several numerical methods have been developed for computing the MEPs, including the Nudged Elastic Band (NEB) method [36] and more recently the string method and its various improvements [18, 19]. These methods are intended to solve the saddle-point problems without any constraint.

In general, many optimization problems may subject to one or more constraints.
There exist variant approaches to solve the constrained problem. Penalty method is one of them and often used in the numerical computation. When the penalty constant goes to infinity, the dynamic of the potential energy by the penalty formulation approaches to the dynamic of the potential energy with the given constraint. However, in general, the penalty method becomes sensitive when the penalty constant becomes larger and larger. Augmented Lagrange multiplier method is a simple modification to the penalty method. It has the advantage that the penalty constant need not be very large. But in the numerical computation by these methods, there is no guarantee to preserve the constraint and ensure the energy law at every time step. Lagrange multiplier method is a popular tool for solving the nonlinear constrained problems. It owes nice mathematical properties and has been extensively studied in many works. In this paper, we adopt the ideas of string methods and take the advantage of the Langrange multiplier to develop a constrained string method for finding the MEP and saddle point which subject to general constraints.

The rest of the Chapter is organized as follows: A brief review of sting method is presented in Section 4.2. In Section 4.3, we describe the mathematical formulation of constrained string method. Numerical analysis is given and a Ginzburg-Landau energy functional is used as an example to illustrate the developed method. In Section 4.4, time discretization of the constrained string method is discussed. We also propose a different approach to implement the constraint by augmented Lagrangian method. In Section 4.5, the numerical algorithm is described for the constrained string method. We use a 3D example to illustrate the developed method and numerical convergence is presented. Moreover, we compare the saddle-point calculation by penalty formulation. It shows that the string method with the penalty formulation can overcome the flaw of the penalty method. Final conclusion is made in Section 4.6.

4.2 String method

The string method is first developed by E, Ren, Vanden-Eijnden [18] in 2002. The main objective of the string method is to find the MEP and saddle points for barrier-crossing events. The method proceeds by evolving strings, i.e., smooth
curves with intrinsic parametrization whose dynamics takes them to the most probable transition path between two metastable regions in configuration space.

Assuming that the potential energy $E(x)$ has at least two minima, at $a$ and $b$. By definition, a MEP is a smooth curve $\varphi^*$ connecting $a$ and $b$ that satisfies

$$\langle \nabla E \rangle^\perp (\varphi^*) = 0 \quad (4.1)$$

where $\nabla E(\varphi)^\perp$ is the component of $\nabla E(\varphi)$ normal to $\varphi$,

$$\langle \nabla E \rangle^\perp (\varphi) = \nabla E(\varphi) - (\nabla E(\varphi), \hat{\tau})\hat{\tau}. \quad \text{(4.2)}$$

Here $\hat{\tau}$ is the unit tangent of the curve $\varphi$ and $(\cdot, \cdot)$ denotes the inner product in the Euclidean space.

The simplest dynamics evolution of a string is written as

$$v_n = -\langle \nabla E \rangle^\perp (\varphi) \quad (4.3)$$

where $v_n$ is the normal velocity of the string. In order to use a suitable form of (4.2) in numerical computation, a particular parametrization of the string can be chosen. Denote that $\varphi(\alpha, t)$ is the instantaneous position of the string, where $\alpha$ is some suitable parametrization, for instance, the simplest one is equal arc-length parametrization where the normalized arc length requires $\alpha = 0$ at $a$ and $\alpha = 1$ at $b$. In this case, Eq.(4.2) must satisfy the constraint

$$(|\varphi_\alpha|)_\alpha = 0 \quad (4.3)$$

So the string method uses the following dynamics form:

$$\varphi_t = -\langle \nabla E \rangle^\perp (\varphi) + \lambda \hat{\tau}, \quad (4.4)$$

where $\hat{\tau} = \frac{\varphi_{\alpha}}{|\varphi_\alpha|}$ and the scalar field $\lambda \equiv \lambda(\alpha, t)$ is a Lagrange multiplier uniquely determined by the choice of parametrization. Because this term does not affect the normal velocity of the curve, changing the parametrization of the curve will not change the evolution of the curve. So we can use a simple interpolation step to realize the term of $\lambda \hat{\tau}$ in the numerical algorithm.
One of the computational complexity is the calculation of the projected force. We need to compute the tangent vector by different ways before and after the saddle point is crossed to ensure the numerical stability, which may lower the accuracy of the method. Recently, E, Ren, Vanden-Eijnden proposed a simplified and improved string method to eliminate the projection step [19].

\[
\varphi_t = -\nabla E(\varphi) + \bar{\lambda} \hat{\tau},
\]

where \( \bar{\lambda} \) is still a Lagrange multiplier to enforce the particular parametrization of the string, which is equivalent to (5.6) with \( \bar{\lambda} = \lambda + (\nabla E(\varphi), \hat{\tau}). \)

In the numerical algorithm, by the simplified version of the string method, the discretized string is composed of a number of images \( \{\varphi_i(t), i = 0, 1, ..., N\} \). Two-step procedure is applied to solve Eq.(4.5), where the evolution of the images along the string is implemented by a time splitting scheme.

First, the discrete images on the string are driven by the full potential force,

\[
(\varphi_i)_t = -\nabla E(\varphi)(\varphi_i)
\]

Then, after a number of steps depending on the accuracy of the constraint (4.3), a simple interpolation/reparametrization step is applied to redistribute the images along the string.

The simplified string method shows the advantage of the numerical computations. It is more stable and more accurate, we refer to [19] for details.

### 4.3 Constrained String Method

In mathematical optimization problems, Lagrange multiplier is often applied to find the extrema of a function of several variables subject to one or more constraints. It is the popular tool in nonlinear constrained optimization. By taking the advantage of Lagrange multiplier, we extend the original string method to the constrained string method.
4.3.1 Lagrange Multiplier

We first define a general constraint as

$$g(\varphi) = 0$$

It could be the volume constraint, surface area constraint, or any other constraints from different objects. Following the dynamics for the string evolution, the equation is given by

$$\varphi_t = -(\nabla E)^\perp(\varphi) + \lambda \nabla g(\varphi) + \bar{\lambda} \hat{\tau}, \quad (4.6)$$

where the scalar parameter $\lambda$ is the Lagrange multiplier for the constraint.

To derive the explicit expression of the Lagrange multiplier $\lambda$, we start by taking the time derivative with respect to $g(\varphi)$

$$\frac{d}{dt}g(\varphi) = \nabla g \varphi_t,$$

$$= \nabla g(-(\nabla E)^\perp(\varphi) + \lambda \nabla g(\varphi) + \bar{\lambda} \hat{\tau}),$$

Notice that the constraint $g(\varphi(\alpha, t)) = 0$, so we have

$$\frac{d}{dt}g(\varphi) = 0, \quad \frac{d}{d\alpha}g(\varphi) = 0$$

Then

$$\lambda |\nabla g|^2 = (\nabla E)^\perp(\varphi) \nabla g(\varphi) + \bar{\lambda} \nabla g(\varphi) \left( \frac{\varphi_\alpha}{|\varphi_\alpha|} \right)$$

$$= (\nabla E)^\perp(\varphi) \nabla g(\varphi)$$

Thus, we arrive the following system:

$$\begin{cases}
\varphi_t = -(\nabla E)^\perp(\varphi) + \lambda \nabla g(\varphi) + \bar{\lambda} \hat{\tau} \\
\lambda |\nabla g|^2 = (\nabla E)^\perp \nabla g(\varphi) \\
(|\varphi_\alpha|)_\alpha = 0
\end{cases} \quad (4.7)$$
We need to point out that the above system is equivalent to

\[
\begin{aligned}
\varphi_t &= -\nabla E(\varphi) + \lambda \nabla g(\varphi) + \hat{\lambda} \hat{\tau} \\
\lambda |\nabla g|^2 &= \nabla E(\varphi) \nabla g(\varphi) \\
(|\varphi_\alpha|)_\alpha &= 0
\end{aligned}
\] (4.8)

So the projection step could still be eliminated as the string method.

### 4.3.2 Energy Law

First, we consider the simple case without any extra constraint and derive the energy law for the string method. Then the dynamic equation is

\[
\varphi_t = -(\nabla E)^\perp(\varphi) \\
\text{s.t. } (|\varphi_\alpha|)_\alpha = 0
\] (4.9)

The second equation in (4.9) is a constraint which satisfies the equal arc-length parametrization. Since changing the parametrization of the curve does not change the curve itself, the second equation will not affect the energy of the curve. So energy law for the string method could be easily obtained by taking the time derivative of \( E(\varphi) \),

\[
\frac{d}{dt} E = \nabla E \varphi_t = \nabla E(-(\nabla E)^\perp(\varphi)) = -|((\nabla E)^\perp(\varphi))|^2
\]

**Proposition 2.** The system (4.7) of the constrained string method preserves the constraint and ensures the energy law.

**Proof.** The system (4.7) is equivalent to the following system:

\[
\begin{aligned}
\varphi_t &= -(\nabla E)^\perp(\varphi) + \lambda \nabla g(\varphi) \\
\lambda |\nabla g|^2 &= (\nabla E)^\perp \nabla g(\varphi)
\end{aligned}
\] (4.10)
subject to $(|\varphi\alpha|)\alpha = 0$. Notice that

$$\frac{d}{dt}g = \nabla g(-(\nabla E)^\perp(\varphi) + \lambda\nabla g(\varphi)) = 0$$

Thus, we have

$$\frac{d}{dt}E = \nabla E(-(\nabla E)^\perp(\varphi) + \lambda\nabla g(\varphi))$$

$$= -|\nabla E(\varphi)|^2 + \lambda(\nabla E(\varphi))^\perp(\nabla g(\varphi) + \lambda(\nabla E, \hat{\tau})\hat{\tau}\nabla g(\varphi))$$

$$= -((\nabla E(\varphi) - \lambda\nabla g(\varphi))^2$$

Here, in the last step,

$$\lambda(\nabla E, \hat{\tau})\hat{\tau}\nabla g(\varphi) = \lambda\frac{|\varphi\alpha|}{|\varphi\alpha|}(\nabla E, \frac{\varphi\alpha}{|\varphi\alpha|})\nabla g(\varphi)\varphi\alpha = 0$$

Thus, both the constraint and energy law are satisfied. Q.E.D.

### 4.3.3 Illustrative Example

We use a Ginzburg-Landau energy functional as an example to show the constrained string method.

$$E(\varphi) = \int\Omega \left(\frac{\epsilon}{2}|\nabla \varphi|^2 + f(\varphi)\right)dx$$

(4.11)

where $f(\varphi)$ is a nonlinear term. To be more precise, we consider the variation of the energy $E(\varphi)$ in the Hilbert space $H^1(\Omega)$ which is the standard $H^1$ Sobolev space on $\Omega$.

Then we use the volume constraint and surface area constraint. For the volume constraint, we define the functional

$$A(\varphi) = \int\Omega \varphi(\alpha,t)d\alpha, \quad \forall \alpha \in [0,1]$$

and for the surface constraint, we define the functional

$$B(\varphi) = \int\Omega \left[\frac{\epsilon}{2}|\nabla \varphi(\alpha,t)|^2 + \frac{1}{4\epsilon}(\varphi(\alpha,t)^2 - 1)^2\right]d\alpha, \quad \forall \alpha \in [0,1]$$
In the sharp interface limit, \( A(\varphi) \) goes to the difference of inside volume and outside volume, and \( B(\varphi) \) is approaching to \( \frac{2\sqrt{2}}{3}area(\Gamma) \), where \( \Gamma \) is the surface.

Following the constrained string method, the dynamic of the string is governed by the following gradient flow equation:

\[
\varphi_t = -\left( \frac{\delta E(\varphi)}{\delta \varphi} \right)^\perp + \lambda_1 \frac{\delta A(\varphi)}{\delta \varphi} + \lambda_2 \frac{\delta B(\varphi)}{\delta \varphi} + \bar{\lambda}\hat{\tau} \tag{4.12}
\]

where the two scalar parameters \( \lambda_1 \) and \( \lambda_2 \) are the Lagrangian multiplier for the two constraints.

Denote

\[
\begin{align*}
w &= -\epsilon \Delta \varphi + \frac{\delta f(\varphi)}{\delta \varphi} \\
g &= -\epsilon \Delta \varphi + \frac{1}{\epsilon}(\varphi^2 - 1)\varphi
\end{align*}
\tag{4.13}
\]

We rewrite the gradient flow equation as

\[
\varphi_t = -w^\perp + \lambda_1 + \lambda_2 g + \bar{\lambda}\hat{\tau} \tag{4.14}
\]

To derive the explicit expression of the Lagrange multipliers \( \lambda_1 \) and \( \lambda_2 \), we start by taking the integration of Eq.(4.14). Since the volume, hence the integral of \( \varphi \), is a constant, we have

\[
\int w^\perp dx = \lambda_1 |\Omega| + \lambda_2 \int g dx + \int \bar{\lambda}(\alpha,t) \frac{\varphi_\alpha}{|\varphi_\alpha|} dx \tag{4.15}
\]

Notice that for \( \forall \alpha \in [0 1] \), \( \int \varphi(\alpha,t) dx = const. \) Then

\[
\frac{d}{d\alpha} \int \varphi(\alpha,t) dx = 0 ,
\]

\[
\implies \int \varphi_\alpha(\alpha,t) dx = 0 .
\]

Since \( \bar{\lambda}(\alpha,t), |\varphi_\alpha| \) are two constants independent of \( x \), we have

\[
\int \bar{\lambda}(\alpha,t) \frac{\varphi_\alpha}{|\varphi_\alpha|} dx = \frac{\bar{\lambda}(\alpha,t)}{|\varphi_\alpha|} \int \varphi_\alpha dx = 0
\]
Then the Eq.(4.15) changes to be

\[ \int w^\bot dx = \lambda_1 |\Omega| + \lambda_2 \int gdx \quad (4.16) \]

Next, we take the time derivative of \( B(\varphi) \):

\[ \int \epsilon \nabla \varphi \cdot \nabla \varphi_t + \frac{1}{\epsilon} (\varphi^2 - 1) \varphi \varphi_t dx = 0 \ , \]

After the integration by part, we have

\[ \int g \varphi_t dx = 0 \quad (4.17) \]

Substitute Eq.(4.14) into the Eq.(4.17), we can get

\[ \int w^\bot gdx = \lambda_1 \int gdx + \lambda_2 \int g^2 dx + \frac{\bar{\lambda}}{|\varphi_\alpha|} \int g \varphi_\alpha dx \quad (4.18) \]

To eliminate the last integration in Eq.(4.18), we take the derivative of \( B(\varphi) \) with respect to \( \alpha \):

\[ \int \epsilon \nabla \varphi \cdot \nabla \varphi_\alpha + \frac{1}{\epsilon} (\varphi^2 - 1) \varphi \varphi_\alpha dx = 0 \ , \]

\[ \Rightarrow \int g \varphi_\alpha dx = 0 \ . \]

So the Eq.(4.18) is rewritten as

\[ \int w^\bot gdx = \lambda_1 \int gdx + \lambda_2 \int g^2 dx \quad (4.19) \]

Collecting (4.14), (4.16) and (4.19) we arrive at the following system:

\[
\left\{ 
\begin{array}{l}
\varphi_t = -w^\bot + \lambda_1 + \lambda_2 g + \bar{\lambda} \hat{r} \\
\int w^\bot dx = \lambda_1 |\Omega| + \lambda_2 \int gdx \\
\int w^\bot gdx = \lambda_1 \int gdx + \lambda_2 \int g^2 dx \\
(\int |\varphi_\alpha| dx)_\alpha = 0
\end{array}
\right.
\quad (4.20)
\]
To show the energy law, we take the time derivative of $E(\varphi)$,

$$\frac{d}{dt} E(\varphi) = \int w \varphi_t dx$$

$$= \int [w(-w^\perp + \lambda_1 + \lambda_2 g)] dx$$

$$= - \int (w^\perp)^2 dx + \lambda_1 \int w^\perp dx + \lambda_2 \int w^\perp g dx$$

$$= - \int [w - \lambda_1 - \lambda_2 g]^2 dx$$

### 4.4 Discretization of constrained string method

#### 4.4.1 Time-discretized constrained string method

Theoretically, we can take the fully implicit scheme and ensure the monotone decreasing of the energy while preserving the constraint. First, we choose a fully implicit scheme for the system (4.10):

$$\begin{cases} 
\varphi^{n+1} - \varphi^n = -\nabla E^\perp(\varphi^{n+1}, \varphi^n) + \lambda \nabla g(\varphi^{n+1}, \varphi^n) \\
\lambda |\nabla g(\varphi^{n+1}, \varphi^n)|^2 = \nabla E^\perp(\varphi^{n+1}, \varphi^n) \nabla g(\varphi^{n+1}, \varphi^n) 
\end{cases} \quad (4.21)$$

where $\nabla E(\varphi^{n+1}, \varphi^n)$ and $\nabla g(\varphi^{n+1}, \varphi^n)$ satisfies the conditions:

$$\begin{cases} 
E(\varphi^{n+1}) - E(\varphi^n) = \nabla E(\varphi^{n+1}, \varphi^n)(\varphi^{n+1} - \varphi^n) \\
g(\varphi^{n+1}) - g(\varphi^n) = \nabla g(\varphi^{n+1}, \varphi^n)(\varphi^{n+1} - \varphi^n) 
\end{cases} \quad (4.22)$$

**Proposition 3.** The system (4.21) for the constrained string method preserves the constraint and ensures the discrete energy law if the conditions (4.22) are satisfied.

**Proof.** The conservation of constraint is straightforward,

$$g(\varphi^{n+1}) - g(\varphi^n) = \nabla g(\varphi^{n+1}, \varphi^n) \cdot [\nabla E^\perp(\varphi^{n+1}, \varphi^n) + \lambda \nabla g(\varphi^{n+1}, \varphi^n)] h$$

$$= 0$$
Furthermore, the discrete energy law is

\[
E(\varphi^{n+1}) - E(\varphi^n) = \nabla E(\varphi^{n+1}, \varphi^n)(\varphi^{n+1} - \varphi^n)
\]

\[
= \nabla E(\varphi^{n+1}, \varphi^n)(-\nabla E^\perp(\varphi^{n+1}, \varphi^n) + \lambda \nabla g(\varphi^{n+1}, \varphi^n))h
\]

\[
= -(\nabla E^\perp(\varphi^{n+1}, \varphi^n) - \lambda \nabla g(\varphi^{n+1}, \varphi^n))^2h
\]

Q.E.D.

4.4.2 Illustrative example

Again, we use the Ginzburg-Landau energy functional with both the volume constraint and surface area constraint as an example to show the time-discretized constrained string method. By (4.20), an implicit numerical system is given as follows:

\[
\begin{aligned}
\frac{\varphi^{n+1} - \varphi^n}{h} &= -w(\varphi^{n+1}, \varphi^n) + \lambda_1 + \lambda_2 g(\varphi^{n+1}, \varphi^n) \\
\int w(\varphi^{n+1}, \varphi^n)dx &= \lambda_1 |\Omega| + \lambda_2 \int g(\varphi^{n+1}, \varphi^n)dx \\
\int w(\varphi^{n+1}, \varphi^n)g(\varphi^{n+1}, \varphi^n)dx &= \lambda_1 \int g(\varphi^{n+1}, \varphi^n)dx + \lambda_2 \int g(\varphi^{n+1}, \varphi^n)^2 dx
\end{aligned}
\]

(4.23)

To satisfy the condition (4.22), we define function \( w \) and \( g \) as

\[
w(\varphi^{n+1}, \varphi^n) = -\frac{\epsilon}{2} \Delta (\varphi^{n+1} + \varphi^n) + \frac{f(\varphi^{n+1}) - f(\varphi^n)}{\varphi^{n+1} - \varphi^n}
\]

\[
g(\varphi^{n+1}, \varphi^n) = -\frac{\epsilon}{2} \Delta (\varphi^{n+1} + \varphi^n) + \frac{1}{4\epsilon}((\varphi^{n+1})^2 + (\varphi^n)^2 - 2)(\varphi^{n+1} + \varphi^n)
\]

Then based on the first two equations of (4.23), we can easily show

\[
A(\varphi^{n+1}) - A(\varphi^n) = \int_\Omega \varphi^{n+1}dx - \int_\Omega \varphi^ndx
\]

\[
= -h \int_\Omega (w(\varphi^{n+1}, \varphi^n)^\perp - \varphi^{n+1} - \lambda_2 g(\varphi^{n+1}, \varphi^n))dx
\]

\[
= 0
\]
By the first and third equations of this system, we have

\[
B(\varphi^{n+1}) - B(\varphi^n) = \int_\Omega (\varphi^{n+1} - \varphi^n) g(\varphi^{n+1}, \varphi^n) dx
\]

\[
= -h \int_\Omega (w(\varphi^{n+1}, \varphi^n) - \lambda_1 - \lambda_2 g(\varphi^{n+1}, \varphi^n)) g(\varphi^{n+1}, \varphi^n) dx
\]

\[
= 0
\]

Furthermore, we have

\[
E(\varphi^{n+1}) - E(\varphi^n) = \int_\Omega w(\varphi^{n+1}, \varphi^n)(\varphi^{n+1} - \varphi^n) dx
\]

\[
= -h \int_\Omega w(\varphi^{n+1}, \varphi^n)(w(\varphi^{n+1}, \varphi^n) - \lambda_1 - \lambda_2 g(\varphi^{n+1}, \varphi^n)) dx
\]

\[
= -h \int_\Omega [w(\varphi^{n+1}, \varphi^n) - \lambda_1 - \lambda_2 g(\varphi^{n+1}, \varphi^n)]^2 dx
\]

which is the discrete analog of the energy law.

### 4.4.3 Augmented Lagrangian method

An alternative way to enforce the constraint is to use an augmented Lagrange multiplier formulation [32]. This is motivated by the use of direct penalty term in the original string method, that is, we may consider applying the original string method to a modified total energy functional of the form

\[
E_M(\varphi) = E(\varphi) + \frac{M}{2} g(\varphi)^2
\]  

(4.24)

with \( M > 0 \) being the penalty constant. The string evolution equation would then become

\[
\varphi_t = -\nabla E(\varphi) - Mg(\varphi) \nabla g(\varphi).
\]  

(4.25)

A direct solution of (5.11) makes the algorithmic implementation much simpler than the system (4.7), but it requires us to choose a large enough \( M \) which increases the stiffness of the equation and to make sure that \( Mg(\varphi) \) converges to the corresponding Lagrange multiplier. In order to circumvent these issues, an augmented Lagrange multiplier approach can be utilized which is based on modifying
the total energy by

\[ E_{ALM}(\varphi) = E(\varphi) + \lambda g(\varphi) + \frac{M}{2} g(\varphi)^2. \]  

\hspace{1cm} \text{(4.26)}

where \( M \) is a finite penalty constant. The augmented Lagrangian method is then implemented via the following iterations:

**Step 1:** Assume \( \lambda_j \) is known, we apply the string method to solve the dynamic equation:

\[ (\varphi_j)_t = -\nabla E(\varphi_j) - \lambda_j \nabla g(\varphi_j) + Mg(\varphi_j) \nabla g(\varphi_j) \]

**Step 2:** Once the solution of \( \varphi_j \) is obtained, we update

\[ \lambda_{j+1} = \lambda_j + Mg(\varphi_j) \nabla g(\varphi_j). \]

Then go back to Step 1 and iterate until convergence.

The augmented Lagrangian method has the advantage that the penalty constant need not be very large and assures the convergence of the Lagrange multiplier and thus the satisfaction of the constraint. The initial estimate of \( \lambda \) and the initial string can be obtained from the direct penalty method with a suitable penalty constant.

### 4.5 Numerical Simulations

#### 4.5.1 Algorithm of constrained string method

If the string is discretized by a number of points, i.e., \( \{\varphi_i\}, i = 1, ..., m, \) we may have many different choices for the reparametrizations. In the string method, after the evolution of the string, a linear or cubic interpolation is used to implement the reparametrization. By the equal arc length or weighted arc length, it is very convenient for the numerical computation. So we can take the advantages of the string method and implement the numerical algorithm for the constrained string method.

We follow the approach proposed by E, Ren, Vanden-Eijnden [19] which is outlined below:
Step 1: Evolution of the string: Assume $\varphi^n_i$, $i = 0, ..., N$ as the positions of the images after $n$ iterations, if we use the explicit Euler scheme, the Lagrange multiplier is calculated by

$$\lambda^{n+1}_i |\nabla g(\varphi^n_i)| = (\nabla E)^\perp(\varphi^n_i) \nabla g(\varphi^n_i)$$

Then the new set of images, $\varphi'$, satisfies the equation:

$$\frac{\varphi'_i - \varphi^n_i}{\Delta t} = -(\nabla E)^\perp(\varphi^n_i) + \lambda^{n+1}_i \nabla g(\varphi^n_i)$$

Step 2: Reparametrization of the string: In the simplest case, we may choose the equal arc-length paramerization.

1. Compute the arc length by the current images,

$$s_0 = 0, \quad s_i = s_{i-1} + |\varphi'_i - \varphi'_{i-1}|, \quad i = 1, 2, ..., N.$$  

The mesh \{\alpha'_i\} is then obtained by normalizing \{s_i\}, i.e., $\alpha^n_i = s_i/s_N$.

2. Apply the linear interpolation to get the new images $\varphi^{n+1}_i$ at the uniform grid points $\alpha_i = i/N$.

3. Once \{\varphi^{n+1}_i\} are obtained, go back to Step 1 and iterate until convergence.

4.5.2 3D example

First we choose a three-dimensional constrained problem to illustrate the developed method. Consider the potential energy $E(x, y, z)$ as

$$E(x, y, z) = (x^2 - 1)^2 + y^2 + 2z^2.$$  \hspace{1cm} (4.27)

with the constraint

$$g(x, y, z) = x^2 + y^2 + z^2 - 1 = 0$$

The potential $E(x, y, z)$ has two minima at $a = (1, 0, 0)$ and $b = (-1, 0, 0)$ respectively. Without the constraint, the exact MEP connecting these two minima
should be the straight line between $a$ and $b$ (Fig.4.1(left)), and the saddle point is $(0, 0, 0)$. Taking into account the constraint $g(x, y, z)$, the exact constrained MEPs connecting two minima are changed to the upper and lower branches of the unit circle in the $(x, y)$ plane, and saddle points are changed to $(0, \pm 1, 0)$.

In our calculation, the string is discretized into $N$ points \( \{X_i = (x_i, y_i), i = 0, 1, ..., N\} \). We used $N$ ranging from 20 to 200 in the numerical experiments. An explicit scheme is applied for the string evolution, and linear interpolation is used to redistribute the discrete points at each time step according to the equal arc length. In Fig.4.1 (right), the calculated constrained MEP is plotted by a red curve, and the energy surface on sphere is highlighted to offer an intuitive understanding.

![Figure 4.1.](image)

Figure 4.1. the exact MEP (left) and the calculated constrained MEP (right), $N = 30$

To show the convergence for various number of images $N$, we compute the error of the converged string versus $N$. Here the error is defined as

\[
\text{error}(N) = \max_i |\sqrt{x_i^2 + y_i^2} - 1|.
\]

In Fig.4.2, it shows that the error decreases linearly because we use the linear interpolation and the explicit Euler method. The result can be improved by the high order scheme such as the cubic spline interpolation and Runge-Kutta method.

### 4.5.3 Calculation of saddle point by penalty formulation

As we discussed in the previous section, another way to enforce the constraint is to use the original string method with the penalty formulation. By adding a penalty
term to the potential energy, we have a modified energy:

\[ E_M(\varphi) = E(\varphi) + \frac{M}{2} g(\varphi)^2 \]

It is known that finding a critical point of the energy function subject to the constraint is not equivalent to finding a critical point of the modified energy with the penalty as \( M \to \infty \). The saddle-point solution calculated by the penalty method may not be the correct one. However, the string method with the penalty formulation could avoid this issue and find the right saddle point. Here, we use the same 3D example to illustrate it and the more general case can be derived in the same way.

The modified energy with a penalty term by (4.27) is given by

\[ E(x, y, z) = (x^2 - 1)^2 + y^2 + 2z^2 + \frac{M}{2} (x^2 + y^2 + z^2 - 1)^2. \]

Taking the calculus of variation, the critical point should satisfy the Euler-Lagrange equation:

\[
\begin{align*}
4x(x^2 - 1) + 2Mx(x^2 + y^2 + z^2 - 1) &= 0 \\
2y + 2My(x^2 + y^2 + z^2 - 1) &= 0 \\
4z + 2Mz(x^2 + y^2 + z^2 - 1) &= 0
\end{align*}
\]

(4.28)
It is easy to see, as $M \to \infty$,

$$(x^2 + y^2 + z^2 - 1) \begin{pmatrix} x \\ y \\ z \end{pmatrix} = 0$$

Then one saddle-point solution is $(0, 0, 0)$, which has a lower energy than the other saddle points $(0, \pm 1, 0)$, but it does not satisfy the constraint. So using directly the penalty formulation to calculate the saddle point may lead to a wrong solution. More generally, the Euler-Lagrange equation given by the penalty formulation is

$$\nabla E(x_M) + Mg(x_M) \nabla g(x_M) = 0$$

Thus, one possible situation where the saddle-point solution $x^*$ of the above equation could be wrong is the case when it satisfies both $\nabla E(x^*) = 0$ and $\nabla g(x^*) = 0$ but $g(x^*) \neq 0$. Yet, there is other possibilities that the penalty formulation fails to find the saddle point, such as $x_M$ diverges or $\nabla E(x_M)$ is not bounded.

The string method with the penalty formulation can overcome this flaw of the penalty method. For instance, in the 3D example, if two ends of the string converge to the local minima, every point on the string will satisfy the constraint when the string converges to the MEP. Then the correct saddle-point solution is identified by the point with the highest energy on the MEP. Otherwise, all points on the string will shrink to a single point $(0, 0, 0)$, which can be easily circumvented by using the initial string where the two end points lie in the two basins of attraction of the minima. Numerical experiments for the 3D example correctly captured this phenomenon.

### 4.6 Conclusion

In this Chapter, we developed a constrained string method to solve the saddle-point problem with general constraints. By taking the advantage of Lagrange multiplier for the constraint, the constrained string method could be easily implemented without changing the intrinsic description of the string method proposed in [18]. Furthermore, numerical analysis is provided for the constrained string method,
including preserving the constraint and ensuring the energy laws. Time discretization for the constrained string method is analyzed and nice approximation features are presented. We also proposed an alternative way to enforce the constraint by using an augmented Lagrangian method, which provides a simpler algorithmic implementation. A 3D example is presented to demonstrate that the constrained string method can successfully find the constrained MEP and the saddle point.
Chapter 5

Simulation of critical nucleus morphology in the conserved solid field

5.1 Introduction

Precipitation is a common, natural process which takes place in a supersaturated solid or liquid solution, i.e., when the composition of a species exceeds its thermodynamic solubility, e.g. during isothermal annealing of a quenched homogeneous alloy within a two-phase field of a phase diagram. It is the basic process that underlies the development of many advanced materials such as high-temperature superalloys and ultralight aluminum and magnesium alloys. The precipitate microstructure (the number density, volume fraction, and morphology) is the dominant factor that determines the mechanical properties of a solid.

One of the main challenges in predicting precipitate microstructures in solids has been the determination of precipitate particle morphology because of the presence of both interfacial energy anisotropy and anisotropic elastic interactions. As the majority of precipitation reactions in solids take place through a nucleation-and-growth mechanism followed by particle coarsening, there are two thermodynamically well-defined morphologies: the morphology of a critical nucleus and the equilibrium morphology of a precipitate particle.
In classical nucleation models, a critical nucleus is usually assumed to be spherical and its radius, the critical size, is determined by a competition between a bulk free energy decrease which is proportional to volume and an interfacial energy increase which is proportional to interfacial area. In a diffuse-interface description or non-classical theory, a critical nucleus is defined as the composition or order parameter fluctuation which has the minimum free energy increase among all fluctuations which lead to nucleation, i.e., the saddle point configuration along the minimum energy path (MEP) between the metastable initial homogeneous phase, a local minimum in the free energy landscape, and the equilibrium phase, the global minimum. Therefore, nucleation of new precipitate particles requires overcoming a thermodynamic barrier. The magnitude of the nucleation barrier, and thus the nucleation rate, or the resulted precipitate particle density, is strongly dependent on the morphology of critical nuclei. On the other hand, following nucleation and growth of precipitate particles, the morphology of precipitate particles during coarsening are generally close to equilibrium. The morphology during coarsening and the precipitate particle density are two of the most critical microstructure information that are needed for predicting the strength of a solid.

There have been extensive studies, particularly numerical simulations, of equilibrium shapes of a precipitate particle in solids using both sharp- and diffuse-interface approaches [71, 46, 47, 56, 68, 73]. More recently, there also have been attempts to predict the morphology of a critical nucleus in a solid taking into account both interfacial energy anisotropy and anisotropic elastic interactions [75, 76, 77, 65]. For example, we showed that one can predict the morphology of a critical nucleus in a system going through a phase transition [75, 76, 77] using a combination of the diffuse-interface (phase-field) description and the minimax algorithm based on the mountain pass theorem. The main objective of this Letter is to report a first attempt to predict the morphology of a critical nucleus as well as the equilibrium morphology of a precipitate simultaneously within the same physical model and mathematical formulation. We will show that the critical nucleus and equilibrium morphology can be dramatically different.

To predict the morphology of a critical nucleus and the equilibrium morphology of a precipitate, we consider a conserved concentration field on a constrained manifold that conserves the average concentration. We extend the string method
We demonstrate that a combination of diffuse-interface description and a constrained string method is able to obtain the morphologies of a critical nucleus and an equilibrium precipitate simultaneously.

As nucleation happens by overcoming the minimum energy barrier, a critical nucleus is defined as the composition fluctuation which has the minimum free energy increase among all fluctuations which lead to nucleation. We thus compute the critical nucleus via the saddle points of the energy functional. This can be done by searching for the most probable transition path, which is also simply called the Minimum Energy Path (MEP), between the local minima of the total energy. The relevant saddle points can be identified with the highest energy point on the MEP. Many numerical methods have been developed for computing the saddle points and MEPs, including the nudged elastic band (NEB) method [36] and more recently the string method and its various improvements [18, 19]. In our past work, we also have used the minimax algorithms based on the mountain pass theorem [75, 77]. In this work, we adopt the ideas of string methods and follow the implementation in a constrained setting which we have analyzed recently [81]. Combined with the diffuse interface formulation, we get a new approach for determining the critical nucleus and the MEP for the conserved composition variable. This approach is capable of finding both the critical nuclei and equilibrium states simultaneously without a priori assumption. The computation involves essentially the calculation of the total free energy functional and its first variation, which can be efficiently carried out in the diffuse interface setting.

The rest of the Chapter is organized as follows. The diffuse interface model of nucleation in solids is introduced in Section 5.2. In Section 5.3, we first briefly recall the string methods developed in [18, 19] and the constrained string method studied in [81], along with algorithmic details for the simulation of the nucleation problem in the conserved field. In Section 5.4, computational results are presented for the case of cubic to cubic transformation to demonstrate the capability of the new approach. More discussions and conclusions are given in Section 5.5.
5.2 Diffuse interface model

Following the Cahn-Hilliard diffuse-interface theory\cite{6}, we consider a conserved field $c$ which describes the concentration distribution in a binary solid. The total free energy, $F_t$, arising from the compositional fluctuation in an initially homogeneous state with $c_0$ is given by

$$F_t(c) = \int_\Omega \left( \frac{1}{2} |A \nabla c|^2 + \delta f(c) \right) \, dx + \beta E_e(c) .$$  \hfill (5.1)

We use a domain $\Omega = (-1, 1)^d$ with $d$ being the space dimension. A periodic boundary condition is used for the composition profile $c$. The period is sufficiently large in comparison with the size of the nucleus and the equilibrium particle, so the effect of boundary conditions is negligible. The gradient energy coefficient $A$ is a constant diagonal tensor in $\Omega$ for isotropic interfacial energy, while for anisotropic interfacial energy, it can be made to be either directionally dependent or dependent on the derivatives of $c$.

The local free energy density increase $\delta f(c)$, arising from a compositional fluctuation around the homogeneous state with composition $c_0$, is given by

$$\delta f(c) = \frac{1}{4\kappa} (c^2 - 1)^2 - \frac{1}{4\kappa} (c_0^2 - 1)^2 - \frac{1}{\kappa} (c - c_0)(c_0^3 - c_0)$$

where $\kappa$ is a coefficient of energy density. The plots of $\delta f = \delta f(c)$ are given in Fig.5.1 for different values of the average composition $c_0$ with $c_s$ being the spinodal composition given by $-\sqrt{3}/3$.

Assuming that the elastic modulus is anisotropic but homogeneous, the mi-
crososcopic elasticity theory of Khachaturyan [42] can be conveniently employed to efficiently calculate the elastic strain energy for simply connected coherent inclusions in a solid. For the case of cubic precipitates in a cubic matrix, the elastic energy contribution can be written as

\[
E_e(c) = \frac{1}{2(2\pi)^d} \int_{\hat{\Omega}} d\mathbf{k} B(\mathbf{n})|\hat{\mathbf{c}}(\mathbf{k}) - \hat{\mathbf{c}}_0(\mathbf{k})|^2 .
\] (5.2)

\(\hat{\mathbf{c}}(\mathbf{k})\) is the Fourier transform of \(c(\mathbf{x})\). The integration in (6.6) is over the reciprocal space \(\hat{\Omega}\) of the reciprocal lattice vector \(\mathbf{n} = \mathbf{k}/|\mathbf{k}| = (n_1, n_2, n_3)\) is the normalized unit vector and \(B(\mathbf{n})\) is given by [42]

\[
B(\mathbf{n}) = 3(c_{11} + 2c_{12})\epsilon_0^2 - \frac{(c_{11} + 2c_{12})^2\epsilon_0^2(1 + 2\zeta s(\mathbf{n}) + 3\zeta^2 n_1^2 n_2^2 n_3^2)}{c_{11} + \zeta(c_{11} + c_{12})s(\mathbf{n}) + \zeta^2(c_{11} + 2c_{12} + c_{44})n_1^2 n_2^2 n_3^2}
\] (5.3)

where \(\zeta = (c_{11} - c_{12} - 2c_{44})/c_{44}\) is the elastic anisotropic factor with \(c_{11}, c_{12}, c_{44}\) being elastic constants in the Voigt’s notation, \(\epsilon_0\) is the lattice mismatch between the nucleating new cubic phase and the parent cubic phase, and \(s(\mathbf{n}) = n_1^2 n_2^2 + n_1^2 n_3^2 + n_2^2 n_3^2\). We set, in particular that, \(\mathbf{n} = 0\) if \(\mathbf{k} = 0\).

Rather than varying the magnitude of lattice mismatch and elastic constants, a factor \(\beta\) is introduced in (6.5) to study the effect of relative elastic energy contribution to chemical driving force on the critical nucleus morphology and equilibrium particle morphology.

For a conserved field, its profile \(c = c(x)\) is subject to the constraint

\[
\int_{\Omega} (c(x) - c_0)dx = 0 .
\] (5.4)

### 5.3 Numerical method

The computation of saddle points or the MEP correponding to the energy functional (6.5) subject to the constraint (6.8) is done here through the constrained string method which is a natural extension of the string methods originally developed by E, Ren, Vanden-Eijnden [18, 19]. We now present briefly the algorithmic procedures. Detailed numerical analysis can be found [81].
5.3.1 Review of string method

The string methods in [18, 19] have been demonstrated as effective approaches to find the MEP and saddle points for barrier-crossing events. The methods proceed by evolving strings, i.e., smooth curves with intrinsic parametrization, to the most probable transition path between two metastable regions in configuration space. Briefly, assuming that the potential energy $V(x)$ has at least two minima, at $a$ and $b$. A MEP is then given by a smooth curve $\varphi^*$ connecting $a$ and $b$ that satisfies

$$\nabla V(\varphi^*)^\perp = 0$$

(5.5)

where $\nabla V(\varphi^*)^\perp$ is the component of $\nabla V(\varphi^*)$ normal to $\varphi^*$. The MEP is computed through an evolution process, namely, if $\varphi(\alpha, t)$ refers to the instantaneous position of the string with $\alpha$ being a suitable parametrization, for instance, the normalized arc-length parametrization with $\alpha = 0$ at $a$ and $\alpha = 1$ at $b$, then the string method is based on the solution of the following dynamic equation for $\varphi = \varphi(\alpha, t)$ [18]:

$$\varphi_t = -\nabla V(\varphi) + \lambda \hat{\tau}.$$  

(5.6)

Here $\hat{\tau}$ is the unit tangent vector of the curve $\varphi$, and the scalar field $\lambda$ is a Lagrange multiplier determined by the choice of parametrization. It has been shown that the equilibrium solution of (5.6) is the exact MEP satisfying (5.5) in [19]. Because the last term in (5.6) does not affect the normal velocity of the curve, a simple interpolation step can be applied to account for the effect of $\lambda \hat{\tau}$ in the numerical algorithm. Furthermore, to make the algorithm simpler and more stable, the projected force calculation $\nabla V^\perp(\varphi)$ can be avoided [19] and (5.6) becomes:

$$\varphi_t = -\nabla V(\varphi) + \bar{\lambda} \hat{\tau},$$  

(5.7)

where $\bar{\lambda}$ is a new Lagrange multiplier. The equation (5.7) is equivalent to (5.6) with the identification $\bar{\lambda} = \lambda + (\nabla V, \hat{\tau})$.

To implement the string method using a discretized string composed of a number of images $\{\varphi_i(t), i = 0, 1, ..., m\}$, a time splitting scheme is often applied which is given by the following two-step procedure is:
**Step 1:** Discrete images on the string are driven by the full potential force: Assume $\varphi^n_i$, $i = 0, ..., m$ as the positions of the images after $n$ iterations, if a simple explicit Euler method is applied, the new set of images, $\varphi'$, satisfies the equation:

$$\frac{\varphi'_i - \varphi^n_i}{\Delta t} = -\nabla V(\varphi_i)$$

**Step 2:** Reparametrization of the string: In the simplest case, we may choose the equal arc-length parametrization.

1. Compute the arc length by the current images,

$$s_0 = 0, \quad s_i = s_{i-1} + |\varphi'_i - \varphi'_{i-1}|, \quad i = 1, 2, ..., m.$$ 

The mesh $\{\alpha'_i\}$ is then obtained by normalizing $\{s_i\}$, i.e., $\alpha^n_i = s_i / s_m$.

2. Apply the linear interpolation to get the new images $\varphi^{n+1}_i$ at the uniform grid points $\alpha_i = i/m$.

3. Once $\{\varphi^{n+1}_i\}$ are obtained, go back to Step 1 and iterate until convergence.

We refer to [19] for more detailed discussions.

### 5.3.2 Constrained string method

The original string method can be extended to solve a constrained problem such as the problem presented here on the study of nucleation in the conserved field during the phase transformations. A constrained string method has been developed to find the MEP on general constrained manifolds [81]. It is essentially the string method with additional Lagrange multipliers. Yet the constraint brings out a technical issue in the numerical implementations. We refer to [81] for more extensive mathematical validation and analysis.

The particular application to the constrained string method for the energy functional (6.5) subject to the simple constraint (6.8) can be briefly described as follows: first, with a Lagrange multiplier treatment of the constraint (6.8), the
evolution of the string is governed by the following dynamic equation is given by

\[
\begin{align*}
\varphi_t &= \nabla \cdot (A \nabla \varphi) - p(\varphi) - q(\varphi) + \lambda + \bar{\lambda} \hat{\tau} \\
\lambda |\Omega| &= \int_{\Omega} (A \Delta \varphi - p(\varphi) - q(\varphi)) \, dx
\end{align*}
\] (5.8)

where

\[
\begin{align*}
p(\varphi) &= \frac{1}{\kappa} (\varphi^3 - \varphi) - \frac{1}{\kappa} (\varphi_0^3 - \varphi_0) \\
q(\varphi) &= \frac{\beta}{(2\pi)^d} \int_{\hat{\Omega}} B(n)(\hat{\varphi}(k) - \hat{\varphi}_0(k)) e^{ikx} \, dk
\end{align*}
\] (5.9)

Yet, an alternative way to enforce the constraint is to use an augmented Lagrange multiplier formulation. This is motivated by the use of direct penalty term in the original string method, that is, we may consider applying the string method in [18, 19] to a modified total energy functional of the form

\[
E_M(\varphi) = E_{\text{total}}(\varphi) + \frac{M}{2} (\int_{\Omega} (\varphi - c_0) \, dx)^2
\] (5.10)

with \(M > 0\) being the penalty constant. The string evolution equation would then become

\[
\varphi_t = \nabla \cdot (A \nabla \varphi) - p(\varphi) - q(\varphi) + M(\int_{\Omega} (\varphi - c_0) \, dx).
\] (5.11)

A direct solution of (5.11) makes the algorithmic implementation much simpler than the system (5.8), but it requires us to choose a large enough \(M\) which increases the stiffness of the equation and to make sure that \(M(\int_{\Omega} (\varphi - c_0) \, dx)\) converges to the corresponding Lagrange multiplier. In order to circumvent these issues, an augmented Lagrange multiplier approach can be utilized which is based on modifying the total energy by

\[
E_{\text{ALM}}(\varphi) = E_{\text{total}}(\varphi) + \lambda \int_{\Omega} (\varphi - c_0) \, dx + \frac{M}{2} (\int_{\Omega} (\varphi - c_0) \, dx)^2.
\] (5.12)

where \(M\) is a finite penalty constant. The augmented Lagrangian method is then implemented via the following iterations:

**Step 1:** Assume \(\lambda_j\) is known, we apply the string method to solve the dynamic
equation:

\[(\varphi_j)_t = \nabla \cdot (A \nabla \varphi_j) - p(\varphi_j) - q(\varphi_j) + \lambda_j + M(\int_{\Omega} (\varphi_j - c_0)dx)\]

**Step 2:** Once the solution of \(\varphi_j\) is obtained, we update

\[\lambda_{j+1} = \lambda_j + M(\int_{\Omega} (\varphi_j - c_0)dx).\]

Then go back to Step 1 and iterate until convergence.

The augmented Lagrangian method has the advantage that the penalty constant need not be very large and assures the convergence of the Lagrange multiplier and thus the satisfaction of the constraint. The initial estimate of \(\lambda\) and the initial string can be obtained from the direct penalty method with a suitable penalty constant.

### 5.3.3 Time and space discretizations

The string evolution equations can be discretized in time using various semi-implicit schemes and time splitting schemes similar to those presented in [18, 19].

For the spatial discretization, with the use of periodic boundary condition, the Fourier spectral method is a natural choice as in our earlier works. It provides an efficient FFT-based implementation while offering superior accuracy. For more detailed numerical analysis of the spatial Fourier discretization, we refer to [77]. Meanwhile, an interesting issue has caught our attention in the numerical computation here. With the conserved field, we noticed that the size of the critical nucleus is very small in comparison to the size of the computational domain. Thus, very high resolution is required in order to obtain the accurate composition profile of the critical nucleus. Naturally, it is possible to use an adaptive Fourier spectral method like the one developed in [22]. Yet in our case, we have found a simpler technique to make numerical simulations more efficient without much overhead. This is done through the variable adjustment of the computational domain along the string. Since the critical nucleus is relatively small and the matrix composition is nearly a constant away from the nucleus, rather than computing on the whole
domain, we may focus on computing the whole composition profile only in the central part of domain while updating the constant profile in the outside matrix. An illustration is given in Fig. 5.2. Instead of computing \( c(x) \) in the whole domain \( \Omega \), we may choose a new function \( (\hat{c}(x), v) \) and the domain \( \hat{\Omega} \), where \( \hat{c}(x) \in \hat{\Omega} \) and \( v \) is a constant which represents the composition outside of \( \hat{\Omega} \). Direct calculation shows that \( (\hat{c}(x), v) \) satisfies the following relation:

\[
\int_{\hat{\Omega}} \hat{c}(x) \, dx + \int_{\Omega/\hat{\Omega}} v \, dx = \int_{\Omega} c(x) \, dx.
\]

Note that, along the string, the composition profiles of the equilibrium solutions vary. In choosing the domain \( \hat{\Omega} \), on other hand, we need to make it small so that it is computational more efficient, and on the other hand, we also need to make it large enough to avoid the loss of accuracy due to the boundary effect. In our implementation, we utilize the fact that the equilibrium composition profiles with the minimum energy are much bigger than that at the saddle point as a general guideline to help us select a larger \( \hat{\Omega} \) at the end of the string close to the minimum while smaller \( \hat{\Omega} \) near the part of the string containing the saddle point. We have found this is sufficient in the two dimensional computations conducted here. In the future, To get more efficient algorithms, it is advantageous to implement an adaptive domain adjustment scheme. Such a method will be considered in our future work, in particular, when the numerical simulation of three dimensional problems.
5.4 Numerical simulations

Based on the model and algorithm described above, we determine both the critical nucleus and equilibrium precipitate. As an illustration, we focus on the two-dimensional example of a cubic to cubic. The computational set-up and the parameters used are as follows. The initial state has a uniform composition with \( c(x) = c_0 \) in \( \Omega \). Then, one end of the string is fixed to be the initial state, and the other end of the string allows to move but it is taken generally within the energy well of the ground state or equilibrium solution. The point with the highest energy on the MEP is identified as the profile corresponding to a critical nucleus. The string is discretized by \( m = 30 \) points, i.e., 29 line segments, and the spatial grid used to compute each point on the string is taken as \( 256 \times 256 \). An adaptive rescaling of the computational domain for points along the string can be implemented to further improve the resolution. Numerical verification was conducted to ensure that sufficient resolution has been achieved. Since both critical nucleus and equilibrium solution are relatively small in comparison to the spatial domain \( \Omega \), their plots are magnified by a factor of 2 in order to get a better view.

In Fig.5.3, we plot the critical nucleus (left) and equilibrium solution (middle) in the presence of the long-range elastic interactions. The MEP (right) shows how the energy changes from the initial state to the final equilibrium state along the string (at the total 30 discrete points). These results correspond to an average composition \( c_0 = -0.9 \), and parameters \( A_1 = A_2 = 1.56 \times 10^{-4}, \kappa = 0.7 \) and \( c_{11} = 250, c_{12} = 150, c_{44} = 200, \epsilon_0 = 0.02, \beta = 0.5 \). One of the interesting observations is the fact that the maximum composition within the critical nucleus is even higher than that of the equilibrium precipitate. For this composition, however, both the critical nucleus and equilibrium precipitate have the same cubic symmetry as a result of elastic energy interactions.

Another example is shown in Fig.5.4 for average composition \( c_0 = -0.88 \). As \( c_0 \) is close to the spinodal point, the interface of critical nucleus becomes more diffuse. The composition value at the center of a critical nucleus decreases and is smaller than the composition of the equilibrium precipitate. As expected, the size of the equilibrium precipitate is larger for \( c_0 = -0.88 \) than for \( c_0 = -0.9 \) as a result of higher supersaturation. Comparing the MEPs for the two compositions,
we can see that the critical energy needed to nucleate a new particle for $c_0 = -0.88$ is lower than that for $c_0 = -0.9$.

In Fig.5.5, the composition profiles of critical nucleus and equilibrium solution are plotted again along x direction for $c_0 = -0.9$ (left) and $c_0 = -0.88$ (right). When $c_0$ is close to $-1$, the critical nucleus clearly shows two phases, and the nucleating composition of critical nucleus is even bigger than that of equilibrium solution. As $c_0$ increases, the composition value at the center of a critical nucleus decreases and is smaller than the equilibrium value for the nucleating phase, which is consistent with the nonclassical nucleation theory.

To examine the effect of elastic energy contributions, we fix the chemical driving force and increase $\beta$ to compute the MEPs. In Fig.5.6 (left), we plot the MEPs with the compositional profiles for the critical nucleus and equilibrium precipitate as inserts for $\beta = 0.5$. At a relatively small elastic energy contribution, both the critical nucleus and the equilibrium precipitate display a cubic symmetry. With higher elastic strain energy contribution, while the critical nucleus maintains the cubic symmetry, the equilibrium precipitate is plate-like with only two-fold symmetry (Fig.5.6 (middle)). As we further increase the elastic energy contribution, for example, $\beta = 1.5$, both the critical nucleus and the equilibrium precipitate
Figure 5.5. composition profile of critical nucleus and equilibrium solution along $x$ direction, $c_0 = -0.9$ (left) and $c_0 = -0.88$ (right).

Figure 5.6. the calculated MEPs for $\beta = 0.5, 1, 1.5$. The critical nuclei and equilibrium solutions are inserted.

exhibit plate-shaped particles (Fig.5.6 (right)). It is also seen in Fig.5.6 that both the nucleation energy barrier and the size of the critical nucleus increase when the elastic energy contribution increases.

The influence of elastic energy contribution on both the morphology of the critical nucleus and the morphology of the equilibrium precipitate can be understood from the competition between interfacial energy and elastic strain energy. The total interfacial energy is proportional to interfacial area between a particle and the matrix while the total elastic strain energy is proportional to the volume of the particle. Since the size of a critical nucleus is significantly smaller than that of an equilibrium precipitate, it is expected that the elastic energy will have a lesser influence on the critical nucleus (assuming the interfacial coherency between the particle and matrix is always maintained during the entire evolution process). Minimization of elastic strain energy leads to plate-shaped particles while minimization of interfacial energy (assuming isotropic) leads to spherical shapes. Therefore, as
the elastic strain energy contribution increases, the shape of the equilibrium precipitate bifurcates first from being cubic to plate-shaped before the critical nucleus does.

We also conduct a series of numerical experiments to verify the convergence of the constrained string method. Interestingly, for the particular constrained problem studied here, it does not need to pick very large $M$ in order to get a convergent Lagrange multiplier from $M \int_\Omega (c(x) - c_0) dx$. In Fig.5.7, we take $c_0 = -0.85$ and choose $M$ from 50 to 500 to compute the Lagrange multiplier corresponding to the constraint along different string positions including the components of $\lambda$ at the saddle point and the equilibrium solution. It shows that as $M$ increases, each component of $\lambda$ approaches to a constant. The relative volume error:

$$\frac{|\int_\Omega (c(x) - c_0) dx|}{|\int_\Omega c_0 dx|}$$

is about 0.017% at the saddle point and 0.68% at the equilibrium solution. This implies that the penalty method already gives very good initial guess for the augmented Lagrange multiplier method.

5.5 Discussion

Nucleation in solids is much more complicated than that in fluids due to the anisotropic interfacial energy and long-range elastic energy interactions. In a recent letter [75], we proposed a diffuse interface approach together with the minimax
method to find the critical nuclei in solid state phase transformations, and the order parameter is used to describe the structure difference in the non-conserved field. Our work here serves to develop similar approach for the computation of critical nuclei with a conserved composition profile. This further extends our understanding for nucleation in more general cases.

First of all, before comparing the critical nucleus with the equilibrium solution, we investigate the equilibrium solutions without elasticity by the developed method. By changing the different average composition $c_0$, the composition profiles for both nucleating phase and parent phase are listed in Table 5.5. We choose two different Fourier modes, $128 \times 128$ and $256 \times 256$. The computational results show that the nucleation composition and matrix composition are close to $+1$ and $-1$. In our calculation, the volume error of the equilibrium solution $c^*$, $\int (c^* - c_0) dx$, is very small and in the order of $10^{-6}$, which implies the solution satisfies the constraint very well.

<table>
<thead>
<tr>
<th>n=128</th>
<th>$c_0 = -0.9$</th>
<th>$c_0 = -0.85$</th>
<th>$c_0 = -0.8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>nucleating composition</td>
<td>1.0178</td>
<td>1.0140</td>
<td>1.0119</td>
</tr>
<tr>
<td>matrix composition</td>
<td>-0.9812</td>
<td>-0.9855</td>
<td>-0.9877</td>
</tr>
<tr>
<td>n=256</td>
<td>$c_0 = -0.9$</td>
<td>$c_0 = -0.85$</td>
<td>$c_0 = -0.8$</td>
</tr>
<tr>
<td>nucleating composition</td>
<td>1.0124</td>
<td>1.0099</td>
<td>1.0085</td>
</tr>
<tr>
<td>matrix composition</td>
<td>-0.9871</td>
<td>-0.9898</td>
<td>-0.9913</td>
</tr>
</tbody>
</table>

Table 5.1. Composition profile of the equilibrium solution for $n = 128$ and $n = 256$

To further understand the elastic energy contributions, Fig.5.8(left) plots critical free energy of formation as a function of average composition $c_0$ for a fixed $\kappa$. The blue circles represent the data points for a critical nucleus with $\beta = 0.125$, and the red circles represent the data points for a critical nucleus without the elasticity contribution. The blue solid curve and red dash curve are the least square fits by cubic polynomials. As expected, with the increase of the average composition, the size of critical nuclei (with cubic symmetry) is reduced and the critical nucleation energy decreases. This dependence is similar to that predicted from the classical nucleation theory for spherical particles. We also notice that, for the given $\kappa$ and elastic energy, the smallest $c_0$ which allows nucleation to happen is $-0.93$, where the energy of equilibrium solution is very close to the initial-state energy (Fig.5.8,
Figure 5.8. Critical nucleation energy with changing driving force (left), MEP with elasticity for \( c_0 = -0.93 \) and without elasticity for \( c_0 = -0.945 \) (right).

If \( c_0 \) is smaller than \(-0.93\), the energy of an equilibrium precipitate becomes higher than the initial homogeneous state, indicating that the initial uniform state could be globally stable so that the elastic energy contribution can prevent the nucleation process from occurring, i.e. coherency strain energy contribution shifts the equilibrium phase boundary. Without elasticity, nucleation can still take place with an even smaller \( c_0 = -0.945 \) (Fig. 5.8, bottom right).

5.6 Conclusion

In summary, we report a new variational approach for computing the morphologies of both a critical nucleus and an equilibrium precipitate without any \textit{a priori} assumption on their shapes. Our calculations reveal that the morphology of a critical nucleus can be dramatically different from the equilibrium one with the effect of elastic energy contributions. Our approach can also be extended to more complex situations such as systems with defects such as dislocations and interfaces, i.e. heterogeneous nucleation.
More applications and future works

The mathematical model and numerical algorithms we have developed could also be applicable to more nucleation phenomena in solids. Some generalizations include the case of the cubic to tetragonal transformations, nucleation for two order parameters. More interesting subjects, such as inhomogeneous nucleation, dynamic simulation of the nucleation process, heterogeneous nucleation, will be considered in the near future.

6.1 Critical nucleus for cubic to tetragonal phase transformation

6.1.1 Elastic energy

There are several crystal lattice rearrangements leading to the various crystallographic orientations (structure domains) of the same martensite phase. For instance, we applied the cubic to cubic transformation within the homogeneous modulus approximation in Chapter 3. Generalizations to the case of cubic to tetragonal transformations is considered in this section.

The cubic to tetragonal crystal lattice rearrangement may be realized by homogeneous strain of three types leading to different orientations of the tetragonal axes, along the [100], [010] and [001] parent phase directions, respectively. These types of strain are described by the matrices
Again we hereby assume that the elastic modulus is anisotropic but homogeneous so we may employ the microscopic elasticity theory of Khachaturyan [42]. For a cubic crystal, the elastic energy formula is written as

\[ E_{\text{elastic}} = \frac{1}{2(2\pi)^d} \int_{\tilde{\Omega}} d\mathbf{k} B(n) |\tilde{\eta}(\mathbf{k}) - \tilde{\eta}_0(\mathbf{k})|^2. \]  

(6.2)

The integration in (6.9) is over the reciprocal space \( \tilde{\Omega} \) of the reciprocal lattice vector \( \mathbf{k}, n = k/|k| = (n_1, n_2, n_3) \) is the normalized unit vector and in three dimensions, and the term \( B(n) \) is given by

\[ B(n) = \lambda_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0 - n_i \sigma_{ij}^0 \Omega_{jl}(n) \sigma_{lm}^0 n_m \]

We choose elastic constants \( c_{11}, c_{12}, c_{44}. \) For a cubic to a tetragonal transition, the stress-free strain is given by the tensor

\[ \epsilon_{ij}^0 = \begin{pmatrix} \epsilon_{11}^0 & 0 & 0 \\ 0 & \epsilon_{11}^0 & 0 \\ 0 & 0 & \epsilon_{33}^0 \end{pmatrix} \]  

(6.3)

By calculation, we can get

\[ B(n) = \bar{B} - \frac{(\sigma_{33}^0)^2}{c_{11}} \Psi(n) \]  

(6.4)

where

\[ \Psi(n) = \left[ \alpha_1^2 + A n_3^2 (1 - n_3^2) - (\alpha_1^2 - 1) n_3^4 + \xi B n_1^2 n_2^2 n_3^2 + 2\xi \alpha_1^2 n_1^2 n_2^1 \right] \times [1 + \xi (c_{11} + c_{12}) (n_1^2 n_2^2 + n_1^2 n_3^2 + n_2^2 n_3^2) + \frac{c_{11} + 2c_{12} + c_{44}}{c_{11}} \xi^2 n_1^2 n_2^2 n_3^2]^{-1} \]

\[ \xi = \frac{c_{11} - c_{12} - 2c_{44}}{c_{44}} \]
\[
\begin{align*}
\alpha_1 &= \frac{\sigma_{11}^0}{\sigma_{33}^0} = \frac{(c_{11} + c_{12})t_1 + c_{12}}{2c_{12}t_1 + c_{11}} \\
t_1 &= \frac{\epsilon_{11}^0}{\epsilon_{33}^0} \\
A &= \frac{c_{11}}{c_{44}} + \alpha_1^2 \frac{c_{11}}{c_{44}} - 2 - 2\alpha_1 \frac{c_{12}}{c_{44}} + 1 \\
B &= \frac{c_{11} + c_{12}}{c_{44}} + 2\alpha_1^2 \frac{c_{11} - c_{44}}{c_{44}} - 4\alpha_1 \frac{c_{12} + c_{44}}{c_{44}} \\
\sigma_{ij}^0 &= \lambda_{ijkl} \epsilon_{kl}^0 = \begin{pmatrix} \sigma_{11}^0 & 0 & 0 \\ 0 & \sigma_{11}^0 & 0 \\ 0 & 0 & \sigma_{33}^0 \end{pmatrix} \\
\sigma_{11}^0 &= (c_{11} + c_{12})\epsilon_{11}^0 + c_{12}\epsilon_{33}^0 \\
\sigma_{33}^0 &= 2c_{12}\epsilon_{11}^0 + c_{11}\epsilon_{33}^0 \\
\bar{B} &= \lambda_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0 = 2\epsilon_{11}^0 \sigma_{11}^0 + \epsilon_{33}^0 \sigma_{33}^0
\end{align*}
\]

### 6.1.2 Discussion of \(B(n)\) in 3D

It should be noticed that all information about the elastic properties of the system and crystallography of the phase transformation is contained in the term \(B(n)\). Finding the shape that minimizes the elastic energy would help us predict the most probable morphology of critical nuclei and precipitates.

To compare the elastic energies for different shapes at a given volume, we consider the three dimensional example for a cuboid particle of dimension \(a\), \(b\) and \(1/(ab)\) with changing aspect ratios. To make the calculation analytically tractable, we carry out the calculation of the elastic energies, albeit in the sharp interface limit of the diffuse interface model. That is, we let \(\eta\) be a Heaviside function with \(\pm 1\) inside and outside the cuboid with its Fourier coefficients given by

\[
\hat{\eta}(k) = \frac{\sin(\pi k_x a) \sin(\pi k_y b) \sin(\pi k_z / (ab))}{\pi^3 k_x k_y k_z}.
\]

Substituting it into (6.9), we can get an estimation of the elastic energy. In the following examples, we show the plots of \(B(n)\) for different eigenstrains and elastic constants. Some constants include \(c_{11} = 250\), \(c_{12} = 150\), and \(c_{44}\) may be varied.
First, we choose the stress-free stain as following:

\[
\epsilon_1^0 = \begin{pmatrix}
3 & 0 & 0 \\
0 & 3 & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

In Fig.6.1, we plot the shapes of \( B(n) \) for two different \( c_{44} \). The \( B(n) \) displays a needle-like shape and the minimum of \( B(n) \) should be in [100] or [010] direction. By calculating the elastic energy in (6.9) with changing aspect ratios of \( a \) and \( b \), we find that the plate-shape inclusion in x-z or y-z plane have a lower energy than the other shapes.

If the stress-fress stain is

\[
\epsilon_2^0 = \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 3
\end{pmatrix}
\]

The \( B(n) \) in Fig.6.7 is more like plate-shape, and it has the minimum along [001] direction. Calculation of the elastic energy shows that the plate-shape inclusion in x-y plane have a lower elastic energy than the others.

In [42], Khachaturyan conclude that the minimum elastic strain energy at a given inclusion volume is attained if the inclusion has an infinite platelet of infinitesimal thickness whose habit is normal to the vector \( n_0 \) minimizing the function \( B(n) \). Our numerical experiments verified this fact, which can help us predict habit planes and orientations of new phase precipitates.

Another example is shown in Fig.6.3. We take the stress-free strain as

\[
\epsilon_3^0 = \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & -2
\end{pmatrix}
\]

and plot the shapes of \( B(n) \). The figure shows that the \( B(n) \) has the minimum along [111] direction. So it reveals that the plate-shape inclusion normal to [111] direction would have a lower elastic energy than the others.
6.1.3 Numerical simulations

Following the diffuse-interface theory of Cahn and Hilliard [6], we consider the conserved field $c$ to describe the concentration distribution in a binary solid. The
total free energy, $F_t$, arising from the compositional fluctuation in an initially homogeneous state with $c_0$ is given by

$$F_t(c) = \int_{\Omega} \left( \frac{1}{2} |A \nabla c|^2 + \delta f(c) \right) \, dx + \beta E_e(c) \quad (6.5)$$

The domain $\Omega = (-1,1)^d$ is used with $d$ being the space dimension. The gradient energy coefficient $A$ is a constant diagonal tensor in $\Omega$ for isotropic interfacial energy, while for anisotropic interfacial energy, it can be made to be either directionally dependent or dependent on the derivatives of $c$.

The local free energy density change $\delta f(c)$ arising from a compositional fluctuation around the homogeneous state with composition $c_0$ is given by

$$\delta f(c) = \frac{1}{4\kappa} (c^2 - 1)^2 - \frac{1}{4\kappa} (c_0^2 - 1)^2 - \frac{1}{\kappa} (c - c_0)(c_0^3 - c_0)$$

where $\kappa$ is a coefficient of energy density.

Assuming that the elastic modulus is anisotropic but homogeneous, the microscopic elasticity theory of Khachaturyan [42] can be most conveniently employed to efficiently calculate the elastic strain energy for the case of a simply connected coherent inclusion in a solid. For the case of cubic precipitates in a cubic matrix, the elastic energy contribution can be written as

$$E_e(c) = \frac{1}{2} \int_{\hat{\Omega}} \frac{d\mathbf{k}B(n)|\hat{c}(\mathbf{k}) - \hat{c}_0(\mathbf{k})|^2}{\overline{B}(\mathbf{n})} \quad (6.6)$$

$\hat{c}(\mathbf{k})$ is the Fourier transform of $c(\mathbf{x})$. The integration in (6.6) is over the reciprocal space $\hat{\Omega}$ of the reciprocal lattice vector $\mathbf{k}$, $\mathbf{n} = \mathbf{k}/|\mathbf{k}| = (n_1, n_2, n_3)$ is the normalized unit vector and $B(\mathbf{n})$ in 2D is written as

$$B(\mathbf{n}) = \overline{B} - \frac{(Ac_{44}n_1^2 + Bc_{44}n_2^2 + Cn_1^2n_2^2)}{c_{44}D(\mathbf{n})} \quad (6.7)$$

where

$$\overline{B} = (c_{11}^0)^2 + (c_{33}^0)^2)c_{11} + 2c_{11}^0c_{33}c_{12};$$

$$\xi = \frac{c_{11} - c_{12} - 2c_{44}}{c_{44}};$$

$$A = (c_{11}^0c_{11} + c_{12}^0c_{33})^2;$$

$$B = (c_{11}^0c_{33} + c_{12}^0c_{11})^2;$$

$$C = (((c_{11}^0)^2 + (c_{33}^0)^2)c_{11} + 2c_{11}^0c_{33}c_{12})c_{11} - c_{12}^2) - c_{44}((c_{11} + c_{12})^2(c_{11}^0 + c_{33}^0)^2);$$
\[ D(n) = c_{11} + \xi(c_{11} + c_{12})n_1^2 n_2^2, \]

c_{11}, c_{12}, c_{44} being elastic constants in the Voigt’s notation. We set, in particular that, \( n = 0 \) if \( k = 0 \).

Rather than varying the magnitude of lattice mismatch and elastic constants, a factor \( \beta \) is introduced to study the effect of relative elastic energy contribution to chemical driving force on the critical nucleus morphology and equilibrium particle morphology. A periodic boundary condition is used for the composition profile \( c \). The period is sufficiently large in comparison with the size of the nucleus and particle to minimize boundary effects.

For a conserved field, its profile \( c = c(x) \) is subject to the constraint
\[
\int_{\Omega} (c(x) - c_0) dx = 0. \tag{6.8}
\]

Based on the model and the algorithm described above, we determine both the critical nucleus and equilibrium precipitate with a conserved composition. As an illustration, we focus on the two-dimensional example of a cubic to cubic transformation within the homogeneous modulus approximation. The computational set-up and the parameters used are as follows. The initial state has a uniform composition with \( c(x) = c_0 \) in \( \Omega \). Then, one end of the string is fixed to be the initial state, and the other end of the string allows to move but it is taken generally within the energy well of the ground state or equilibrium solution. The point with the highest energy on the MEP is identified as the profile corresponding to a critical nucleus. The string is discretized by \( m = 30 \) points and the spatial simulation grid is maintained as \( 256 \times 256 \). Numerical verification was conducted to ensure that there is enough resolution. Since both critical nucleus and equilibrium solution are relatively small in comparison to the computational domain, their plots are magnified by a factor of 2 in order to get a better view.

In the following figures, we take the average composition \( c_0 = -0.86 \), and parameters \( A_1 = A_2 = 1.56 \times 10^{-4}, \kappa = 1.5 \) and \( c_{11} = 250, c_{12} = 150, c_{44} = 200, \epsilon_{11}^0 = 0.02, \epsilon_{33}^0 = -0.02 \). For the first example in Fig.6.4, we choose \( \beta = 1 \) and plot the critical nucleus (left) and equilibrium solution (middle) in the presence of the long-range elastic interactions. The MEP (right) is included to demonstrate the
The energy changes from the initial state to the final equilibrium state. It shows that the critical nucleus is small and the equilibrium precipitate displays a diamond shape. The composition value at the center of a critical nucleus is also smaller than the composition of the equilibrium precipitate.

Another example is shown in Fig. 6.5 for $\beta = 2.5$. With higher elastic strain energy contribution, while the critical nucleus maintains the cubic symmetry, the equilibrium precipitate is plate-like with only two-fold symmetry. As we further increase the elastic energy contribution, for example, $\beta = 3$ in Fig. 6.6, both the critical nucleus and the equilibrium precipitate exhibit plate-shaped particles.

From the numerical examples for cubic to tetragonal phase transformation in the conserved field, similar as cubic to cubic transformation, we can see that the
elastic energy plays an important role to determine the morphologies of both the critical nucleus and the equilibrium solution. For the same $\beta$, the influence of elastic energy on the critical nucleus and equilibrium solution may be different. Relatively small elastic energy contribution produces both the critical shape and equilibrium shape with cubic symmetry. When the elastic energy contribution increases to a certain value, the equilibrium solution becomes plate-shape while the critical shape retains cubic symmetry. This is because of the competition between the elastic energy and interfacial energy. The equilibrium solution prefers plate shape because the elastic energy dominates the interfacial energy. But for the critical nucleus, the interfacial energy is still comparable with the elastic energy since the size of critical nucleus is relatively small in comparison with the equilibrium solution. If we keep increasing the elastic energy contribution, the size of critical nucleus increases, so it is energetically more favorable to form plate shapes for both critical nucleus and equilibrium solution.

6.2 Nucleation for two order parameters in solids

6.2.1 Chemical free energy

In the diffuse-interface model, we consider the cubic to tetragonal transformation. So the two orientation domains of the tetragonal phase can be described by two long-range order parameter fields:

$$\eta_1(x), \eta_2(x)$$

Each of order parameter fields characterizes the shape, size, and spatial distribution of one of the two orientation domains.

The total free energy contains a bulk free energy, $f(\eta_1, \eta_2)$, and non-local gradient terms, i.e.,

$$E_{\text{total}} = \int_{\Omega} \left[ \frac{1}{2} (\alpha_1 |\nabla \eta_1(x)|^2 + \alpha_2 |\nabla \eta_2(x)|^2) + f(\eta_1(x), \eta_2(x)) \right] dx$$

where $\alpha_1, \alpha_2$ are gradient energy coefficients.

The bulk free energy is usually approximated by a Landau-type polynomial
expansion following the symmetry operations with respect to the parent phase. Here we choose an expansion with terms up to sixth order, so it is written as

\[ f(\eta_1, \eta_2) = \frac{a}{2}(\eta_1^2 + \eta_2^2) - \frac{b}{4}(\eta_1^4 + \eta_2^4) + \frac{c}{6}(\eta_1^2 + \eta_2^2)^3 \]

In order to choose some suitable parameters, a couple of conditions should be satisfied:

\[ f_x(\pm1, 0) = 0, \quad f_y(0, \pm1) = 0 \]

\[ f(\pm1, 0) < f(0, 0) = 0 \]

So it turns out

\[ a - b + c = 0; \quad \frac{a}{2} - \frac{b}{4} + \frac{c}{6} < 0 \]

One example is shown in Fig.6.7. Here we take \( a = 2, b = 19, c = 17 \). It is easy to see that \( f(0, 0) = 0 \) (local minimum), and \( f(\pm1, 0) = f(0, \pm1) < 0 \) (global minimum). So the initial state is \( (\eta_1, \eta_2) = (0, 0) \), and the final state would be \( (\eta_1, \eta_2) = (\pm1, 0) \) or \( (0, \pm1) \) which depends on different orientation domains. Meanwhile, there exists an energy barrier along the energy path.

![Figure 6.7. Free energy surface, contour, free energy for one single domain](image)

### 6.2.2 Elastic energy for two order parameters

For a single order parameter, the elastic energy is written as

\[ E_{\text{elastic}} = \frac{1}{2(2\pi)^d} \int_{\hat{\Omega}} d\mathbf{k} B(\mathbf{n}) |\hat{\eta}(\mathbf{k}) - \hat{\eta}_0(\mathbf{k})|^2. \quad (6.9) \]

The integration in (6.9) is over the reciprocal space \( \hat{\Omega} \) of the reciprocal lattice vector \( \mathbf{k} \), \( \mathbf{n} = \mathbf{k}/|\mathbf{k}| = (n_1, n_2, n_3) \) is the normalized unit vector and in three dimensions,
and the term $B(n)$ is given by

$$B(n) = \lambda_{ijkl} \epsilon_{ij}^0 \epsilon_{kl}^0 - n_i \sigma_{ij}^0 \Omega_{jl}(n) \sigma_{lm}^0 n_m$$

We choose elastic constants $c_{11}, c_{12}, c_{44}$. If the crystal lattice rearrangement is from a cubic to a tetragonal phase the stress-free strain is given by the tensor

$$\epsilon_{ij}^0 = \begin{pmatrix} \epsilon_{11}^0 & 0 & 0 \\ 0 & \epsilon_{11}^0 & 0 \\ 0 & 0 & \epsilon_{33}^0 \end{pmatrix}$$ (6.10)

From the previous section, we have $B(n)$ in 3D:

$$B(n) = \bar{B} - \frac{(\sigma_{33}^0)^2}{c_{11}} \Psi(n)$$ (6.11)

where

$$\Psi(n) = [\alpha_1^2 + An_3^2(1 - n_2^2) - (\alpha_1^2 - 1)n_3^4 + \xi Bn_1^2n_2^2n_3^2 + 2\xi \alpha_1 n_1^2n_2^2]$$

$$\times [1 + \xi \frac{c_{11} + c_{12}}{c_{11}}(n_1^2n_2^2 + n_1^2n_3^2 + n_2^2n_3^2) + \frac{c_{11} + 2c_{12} + c_{44}}{c_{11}} \xi^2 n_1^2n_2^2n_3^2]^{-1}$$

$$\xi = \frac{c_{11} - c_{12} - 2c_{44}}{c_{44}}$$

$$\alpha_1 = \frac{\sigma_{11}^0}{\sigma_{33}^0} = \frac{(c_{11} + c_{12})t_1 + c_{12}}{2c_{12}t_1 + c_{11}}$$

$$t_1 = \frac{\epsilon_{11}^0}{\epsilon_{33}^0}$$

$$A = \frac{c_{11}}{c_{44}} + \alpha_1^2 \frac{c_{11}}{c_{44}} - 2 - 2\alpha_1 \left( \frac{c_{12}}{c_{44}} + 1 \right)$$

$$B = \frac{c_{11} + c_{12}}{c_{44}} + 2\alpha_1^2 \frac{c_{11} - c_{44}}{c_{44}} - 4\alpha_1 \frac{c_{12} + c_{44}}{c_{44}}$$

$$\sigma_{ij}^0 = \lambda_{ijkl} \epsilon_{kl}^0 = \begin{pmatrix} \sigma_{11}^0 & 0 & 0 \\ 0 & \sigma_{11}^0 & 0 \\ 0 & 0 & \sigma_{33}^0 \end{pmatrix}$$

$$\sigma_{11}^0 = (c_{11} + c_{12})\epsilon_{11}^0 + c_{12}\epsilon_{33}^0$$

$$\sigma_{33}^0 = 2c_{12}\epsilon_{11}^0 + c_{11}\epsilon_{33}^0$$
\[ \bar{B} = \lambda_{ijkl} \varepsilon_{ij}^0 \varepsilon_{kl}^0 = 2 \varepsilon_{11}^0 \sigma_{11}^0 + \varepsilon_{33}^0 \sigma_{33}^0 \]

For two order parameters, the stress-free strain is

\[ \varepsilon_{ij}^0(x) = \sum_{p=1}^{2} \varepsilon_{ij}^0(p) \eta_p^2(x) \]

where \( \varepsilon_{ij}^0 \) is constant. The elastic strain is the difference between the total strain and the stress-free strain, i.e.

\[ \varepsilon_{ij}^{el}(x) = \varepsilon_{ij}(x) - \varepsilon_{ij}^0(x) \]

In the homogeneous modulus approximation, the elastic stress field is related to the elastic strain through

\[ \sigma_{ij} = c_{ijkl} \varepsilon_{ij}^{el} = c_{ijkl}(\varepsilon_{ij}(x) - \sum_{p=1}^{2} \varepsilon_{ij}^0(p) \eta_p^2(x)) \]

Following Khachaturyan’s theory, the total strain \( \varepsilon_{ij} \) may be represented as the sum of homogeneous and heterogeneous strains:

\[ \varepsilon_{ij} = \bar{\varepsilon}_{ij} + \delta \varepsilon_{ij} \]

The homogeneous strain is written as the local displacements:

\[ \delta \varepsilon_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial r_j} + \frac{\partial u_j}{\partial r_i} \right) \]

Then the equilibrium equation for local displacements is

\[ c_{ijkl} \frac{\partial^2 u_i}{\partial r_j \partial r_l} = \sum_{p=1}^{2} \sigma_{ij}^0(p) \frac{\partial (\eta_p^2)}{\partial r_j} \]

where \( \sigma_{ij}^0(p) = c_{ijkl} \varepsilon_{kl}^0(p) \).

We use the fact \( \int \delta \varepsilon_{ij}(x) dx = 0 \) and choose \( \bar{\varepsilon}_{ij} = 0 \). So the form of the elastic energy formula of a multi-domain mixture can be expressed as
\[ E_{\text{elastic}} = \int \frac{1}{2} c_{ijkl} [\varepsilon_{ij} + \delta \varepsilon_{ij} - \sum_{p=1}^{2} \varepsilon_{ij}^0(p) \eta^2_p(x) + \sum_{q=1}^{2} \delta \varepsilon_{kl} - \sum_{q=1}^{2} \varepsilon_{kl}^0(q) \eta^2_q(x)] dx \]

\[ = \frac{1}{2} c_{ijkl} \sum_{p,q=1}^{2} \varepsilon_{ij}^0(p) \varepsilon_{kl}^0(q) \int \eta^2_p(x) \eta^2_q(x) dx - \frac{1}{2} \sum_{p,q=1}^{2} \left( \varepsilon_{ij}^0(p) \eta^2_p(0) \eta^2_q(0) \right) \int \eta^2_p(x) \eta^2_q(x) dx \]

\[ = \frac{1}{2} \sum_{p,q=1}^{2} \bar{B}_{pq} \int \eta^2_p(x) \eta^2_q(x) dx - \frac{1}{2} \sum_{p,q=1}^{2} \int \frac{dk}{(2\pi)^3} B_{pq}(\mathbf{n}) (\eta^2_p(k) \eta^2_q(k)) \]

where

\[ B_{pq}(\mathbf{n}) = n_i \sigma_{ij}^0(p) \Omega_{jk}^0(q) n_k \]

and \( \Omega_{ij}(\mathbf{n}) \) is a green function tensor which is inverse to the tensor \( \Omega_{ij}^{-1}(\mathbf{n}) = c_{ijkl} n_k n_l \).

If the eigenstrain is given by

\[ \varepsilon^0(1) = \varepsilon_0 \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} ; \quad \varepsilon^0(2) = \varepsilon_0 \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \]

we can derive more explicit form of the elastic energy.

\[ \bar{B}_{11} = \bar{B}_{22} = 2c_0^2(c_{11} - c_{12}) \]

\[ \bar{B}_{12} = \bar{B}_{21} = -\bar{B}_{11} \]

\[ B_{11}(\mathbf{n}) = B_{22}(\mathbf{n}) = -\frac{c^2_0(c_{11} - c_{12})(c_{44} + 2(c_{11} + c_{12})n_1^2n_2^2)}{c_{44}D(\mathbf{n})} \]

\[ B_{12}(\mathbf{n}) = B_{21}(\mathbf{n}) = -B_{11}(\mathbf{n}) \]

\[ D(\mathbf{n}) = c_{11} + \xi(c_{11} + c_{12})n_1^2n_2^2; \quad \xi = \frac{c_{11} - c_{12} - 2c_{44}}{c_{44}} \]

Thus, the total energy for two order parameters is

\[ E_{\text{total}} = \int_{\Omega} \left[ \frac{1}{2}(\alpha_1 | \nabla \eta_1(x) |^2 + \alpha_2 | \nabla \eta_2(x) |^2) + f(\eta_1(x), \eta_2(x)) \right] dx + \beta \cdot E_{\text{elastic}} \]
where

\[ E_{\text{elastic}} = \frac{1}{2} \sum_{p,q=1}^{2} \bar{B}_{pq} \int \eta_p^2(x)\eta_q^2(x)dx - \frac{1}{2} \sum_{p,q=1}^{2} \int \frac{dk}{(2\pi)^3} B_{pq}(\vec{n})(\hat{\eta}_p^2)(k)(\hat{\eta}_q^2)(k) \]

6.2.3 Numerical simulations

Based on the model and the algorithm, we compute the critical nuclei for two order parameters in a non-conserved field. As an illustration, we focus on the two-dimensional example of a cubic to tetragonal transformation within the homogeneous modulus approximation. The computational set-up and the parameters used are as follows. One end of the string is fixed to be the initial state, and the other end of the string allows to move but it is taken generally within the energy well of the ground state or equilibrium solution. The point with the highest energy on the MEP is identified as the profile corresponding to a critical nucleus. The string is discretized by \( m = 50 \) points and the spatial simulation grid is maintained as \( 128 \times 128 \). Some other parameters are \( \alpha_1 = \alpha_2 = 0.039, a = 0.25, b = 16, c = 15.75, c_{11} = 250, c_{12} = 150, c_{44} = 200, \epsilon_0 = 0.01 \). Numerical verification was conducted to ensure that there is enough resolution.

In Fig.6.8, we plot the critical nucleus and equilibrium solution for two order parameters without elasticity, i.e., \( \beta = 0 \). Only one order parameter \( \eta_1 \) appears in the critical nucleus, and \( \eta_2 = 0 \). For the equilibrium state, two tetragonal variants \( \eta_1 \) and \( \eta_2 \) show the twin structure. In Fig.6.9, we choose \( \beta = 0.5 \) to study the effect of the elastic energy contribution. With the elasticity, the critical nucleus grows bigger and critical nucleation energy increases. The equilibrium state diffuses more and the maximum value in \( \eta_1 \) and \( \eta_2 \) is lower than that for \( \beta = 0 \).

In order to study the morphology of critical nuclei in the presence of the interaction between two different order parameters, we choose a different initial string to compute the critical nucleus and equilibrium solution. In Fig.6.10, we plot the critical nucleus and equilibrium solution for two order parameters without elasticity. The critical nucleus shows a two-variant twinned structure and the equilibrium one appears a polytwin structure consisting of alternating layers of two tetragonal variants. Then we take \( \beta = 1 \) in Fig.6.11. The critical nucleus keeps the twinned structure and becomes a bigger one, and the equilibrium state changes as similar
Figure 6.8. Critical nucleus and equilibrium state for $\beta = 0$

Figure 6.9. Critical nucleus and equilibrium state for $\beta = 0.5$

as the previous example.

Figure 6.10. Critical nucleus and equilibrium state for $\beta = 0$
Future works

Our recent works on the mathematical modeling and computational algorithms opened some new research directions and provided useful tools for the analysis of the nucleation phenomenon in general.

6.3.1 Dynamic simulation of the nucleation process

The conventional phase field dynamic equations, including the Cahn-Hilliard equation and the Allen-Cahn equation (also known as the time-dependent Ginzburg Landau equation), can only describe dissipative processes because the time derivatives of the total energy functional, by integrating the dynamic equations, are always non-positive. Modeling nucleation process thus requires incorporation of additional physical terms that describe thermally activated processes.

We are exploring the combination of our variational calculations with the stochastic modeling such as kinetic Monte Carlo method, transition state theory and other techniques so as to more efficiently model and simulate such multiscale processes.

6.3.1.1 Langevin force approach

The Langevin force approach is an analogue to the treatments for Brownian motion in statistical mechanics, which mimics the thermal interactions between the system and the environment in terms of phenomenological force terms. The Langevin force
terms are incorporated directly into the phase field dynamics as
\begin{align}
\frac{\partial c(x,t)}{\partial t} &= \nabla \cdot M_c \nabla \frac{\delta E_{\text{total}}(c)}{\delta c} + \xi_c(x,t) \tag{6.12} \\
\frac{\partial \eta(x,t)}{\partial t} &= -M_\eta \frac{\delta E_{\text{total}}(\eta)}{\delta \eta} + \xi_\eta(x,t) \tag{6.13}
\end{align}

where \(c\) and \(\eta\) represent a conserved field and a non-conserved field, respectively. The Langevin noise terms, in the simplest forms, are assumed uncorrelated in both time and space. This requires their first and second moments to satisfy
\begin{align*}
<\xi_c(x,t)> &= 0, \quad <\xi_\eta(x,t)> = 0 \\
<\xi_c(x,t)\xi_c(x',t')> &= -2k_B T M_c \delta(t - t')\nabla^2 \delta(x - x') \\
<\xi_\eta(x,t)\xi_\eta(x',t')> &= 2k_B T M_\eta \delta(t - t')\delta(x - x')
\end{align*}
and yields a Gaussian distribution.

By adding the Langevin noise terms in (6.12) and (6.13), it provides an elegant treatment of nucleation. However, this becomes computationally expensive, since it requires sampling at a very high frequency in order to observe nucleation events, which are very rare.

### 6.3.1.2 Explicit nucleation algorithm

Instead of the Langevin force approach, the explicit nucleation algorithm was developed in [67] in order to adapt the phase field model to conditions of concurrent nucleation and growth. This was accomplished through a hybrid model, in which stochastic nucleation events were explicitly introduced into the Phase Field model. As a demonstration, a simple nucleation model was applied to determine local nucleation rates as functions of local supersaturation. These rates were then used to determine the behavior of the nucleation events. The approach included two algorithms which alternate, one for nucleation and one for growth and coarsening.

**A. Nucleation:** The classical nucleation theory is applied to determine the critical nuclei in [67]. The sample is grided into individual cells and the same cells are used for the phase field model. Nucleation and growth take place by a cyclic process, by which a nucleation phase is followed by a growth phase. During the
nucleation phase, nuclei are introduced into individual cells randomly, but with a 
mean formation rate that matches the desired nucleation rate.

As a result, prior applications of the classical nucleation theory to solid state 
transformations typically make assumptions on the shape of a nucleus as an a 
priori, which limits the explicit nucleation algorithm to be only applicable to the 
simple nucleation models. In order to simulate more complicated nucleation pro-
cesses such as solid state phase transformation, we could apply the phase field 
model combined with efficient numerical algorithm, including minimax method in 
[75] and constrained string method in [81], to predict the critical nuclei morpholo-
gies and calculate the accurate nucleation rate without any a priori assumption.

To improve the explicit nucleation algorithm, the nucleation in a conserved field 
is presented as an example. We first compute the critical nuclei in the conserved 
field based on the phase field model and the constrained string method in [79]. 
Once we get the compositional profile of the critical nucleus for the different average 
composition, we can then calculate the nucleation rate which is more accurate than 
that computed by the classical nucleation theory.

**B. Growth and coarsening:** The phase field method is applied to model 
growth and coarsening. Taking into account the anisotropic interfacial energy 
and anisotropic elastic energy contributions, the Cahn-Hilliard equation and the 
Allen-Cahn equation can be written as

\[
\frac{\partial c(x, t)}{\partial t} = \nabla \cdot M_c \nabla \left[ \frac{\delta f}{\delta c} - k_c \Delta c + \frac{\delta E_{\text{elastic}}}{\delta c} \right] \tag{6.14}
\]

\[
\frac{\partial \eta(x, t)}{\partial t} = -M_\eta \left[ \frac{\delta f}{\delta \eta} - k_\eta \Delta \eta + \frac{\delta E_{\text{elastic}}}{\delta \eta} \right] \tag{6.15}
\]

To solve the Cahn-Hilliard equation or Allen-Cahn equation, we may apply the 
semi-implicit Fourier-spectral method in [8]. The time variable is discretized by 
using semi-implicit schemes which allow much larger time step sizes than explicit 
schemes; the space variables are discretized by using a Fourier-spectral method 
whose convergence rate is exponential in contrast to second order by a usual finite-
difference method.
6.3.1.3 Numerical simulation

Working with Dr. Chen’s group in the Department of Materials Science and Engineering at Pennsylvania State University, we have done some preliminary works for the dynamic simulation of the nucleation process. As an illustration, we first focus on the two-dimensional example without elasticity. Thus, the total free energy in the phase field model is

\[
\Delta E_{\text{total}}(c) = \int_{\Omega} \left( \delta f(c) + \frac{\kappa}{2} (\nabla c(x,t))^2 \right) dx
\]  

(6.16)

here, the chemical free energy density

\[
\delta f(c) = \left[ \frac{B}{4} (c(x) - 0.5)^4 - \frac{A}{2} (c(x) - 0.5)^2 \right] - \left[ \frac{B}{4} (c_0 - 0.5)^4 - \frac{A}{2} (c_0 - 0.5)^2 \right] - (c(x) - c_0) (B(c(x) - 0.5)^3 - A(c(x) - 0.5))
\]

where \( A = 7 \) and \( B = 34.57 \), and interfacial energy coefficient is \( \kappa = 0.0781 \).

The computational set-up and the parameters used are as follows. One end of the string is fixed to be the initial state, and the other end of the string allows to move but it is taken generally within the energy well of the ground state or equilibrium solution. The point with the highest energy on the MEP is identified as the profile corresponding to a critical nucleus. The domain of each computational cell is \([-11] \times [-11]\). The string is discretized by \( m = 60 \) points and the spatial simulation grid is maintained as \( 64 \times 64 \).

In Fig.6.12, we capture the composition profile for the evolution process at the time \( t = 20, 100 \) and 190. At the early stage, there are only a few of nuclei generated due to the low nucleation rate. Then these nuclei grow up and more nuclei are generated as time increases. In the future, we will invest the statistics of the nucleation process and will also take into account the anisotropic elastic energy for a cubic to cubic/tetragonal transformation within the homogeneous modulus approximation.
6.3.2 Inhomogeneous nucleation in solid states

In an elastically homogeneous solid with an arbitrary microstructure, Khachaturyan’s microelasticity theory [42] provides an efficient approach to calculate the elastic energy. It has been applied to study the effect of elastic energy on microstructure evolution during various structural phase transformations [7]. For systems with weak elastic inhomogeneity, first-order approximations have been employed to solve the mechanical equations. However, the numerical solution to the mechanical equilibrium equation becomes significantly more complicated for microstructures with strong elastic inhomogeneity. Based on the phase field model, we are going to explore the inhomogeneous nucleation in solid state phase transformation and invest the effect of strong elastic inhomogeneity on the morphology of the critical nucleus in solid states.

6.3.2.1 Mechanical equilibrium equation

We describe a general description of a system consisting of a solid phase and a gas phase. The gas phase represents voids or cracks where elastic constants are modeled as zero. We assume that the solid phase is a binary solid solution with a compositional inhomogeneity \( c = c(x) \) which represents the mole fraction of solutes at the position \( x \), and the local elastic modulus tensor is a linear function of the compositional inhomogeneity. Therefore, the local elastic modulus tensor is given by

\[
\lambda_{ijkl}(x) = \lambda_{ijkl}^0 + \lambda'_{ijkl}\delta c(x)
\]

in the solid phase, where \( \delta c(x) = c(x) - c_0 \), \( \lambda_{ijkl}^0 \) is an elastic modulus tensor for the homogeneous solid solution with the composition \( c_0 \), and \( \lambda'_{ijkl} \) is a constant tensor.
representing the elastic inhomogeneity within the binary solid solution. We assume
\( \delta c(x) \) is constructed in such a way that the elastic modulus tensor experiences a
smooth transition to degeneracy over a thin interface between the solid and gas
phases. In addition, we assume that the local stress-free strain tensor can be
described in terms of the compositional inhomogeneity \( \varepsilon^c_{ij}(x) \). If the variation of the
stress-free lattice parameter \( a \) with respect to the composition obeys the Vegard’s
law, the local stress-free strain associated with the compositional inhomogeneity
is given by
\[
\varepsilon^c_{ij}(x) = \varepsilon_0 \delta c(x) \delta_{ij},
\]
where \( \varepsilon_0 \) is the composition expansion coefficient of the lattice parameter and
\( \delta_{ij} \) is the Kronecker-Delta function. Most crystal defects such as dislocations,
and boundaries and cracks can be described by their corresponding spatially
dependent stress-free strain \( \varepsilon^{def}_{ij}(x) \). Therefore, the total stress-free strain tensor
\( \varepsilon^0_{ij}(x) \) associated with the compositional inhomogeneity and distributed defects is
\[
\varepsilon^0_{ij}(x) = \varepsilon^c_{ij}(x) + \varepsilon^{def}_{ij}(x)
\]
Let us use \( \varepsilon_{ij}(x) \) to denote the total strain measured with respect to a reference
lattice and assume linear elasticity. The Hooke’s law gives the local elastic stress,
\[
\sigma_{ij} = (\lambda \varepsilon_{ijkl} + \lambda' \delta c(x)) (\varepsilon_{kl}(x) - \varepsilon^0_{kl}(x)).
\]
During the evolution of microstructure, since the mechanical equilibrium with
respect to elastic displacements is usually established much faster than any other
physical processes, for any given composition distribution, the system is always at
a mechanical equilibrium,
\[
\frac{\partial \sigma_{ij}}{\partial x_j} = 0,
\]
where \( x_j \) is the \( j \)th component of the position vector \( x \). The total strain \( \varepsilon_{ij} \) may
be represented as the sum of homogeneous and heterogeneous strains:
\[
\varepsilon_{ij} = \bar{\varepsilon}_{ij} + \delta \varepsilon_{ij},
\]
The homogeneous strain is defined in such a way so that

\[ \int_{\Omega} \delta \varepsilon_{ij} d\mathbf{x} = 0. \]

The heterogeneous strain is related to the local displacement field \( \{v_k\} \) by the usual elasticity relation,

\[ \delta \varepsilon_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right). \]

Thus, the mechanical equilibrium equation (6.17) could be written as

\[ \left[ \lambda^0_{ijkl} \frac{\partial^2}{\partial x_j \partial x_l} + \lambda'_{ijkl} \frac{\partial}{\partial x_j} (\delta c(x) \frac{\partial}{\partial x_l}) \right] u_k(x) = \frac{\partial}{\partial x_j} \left[ \lambda^0_{ijkl} + \lambda'_{ijkl} \delta c(x) \right] (\varepsilon^0_{kl}(x) - \bar{\varepsilon}_{ij}). \]

(6.18)

Then, the determination of the equilibrium elastic field for an elastically inhomogeneous solid is reduced to solving the mechanical equilibrium equations (elasticity equations) (6.18) subject to appropriate boundary conditions, and in particular, periodic boundary conditions in this paper. Please notice that in the gas phase, both the left-hand and the right-hand sides of (6.18) are zero, and thus the uniqueness of the solution to (6.18) cannot be expected to hold in the gas phase.

### 6.3.2.2 Iterative-perturbation scheme

In [74], a simple iterative-perturbation scheme was proposed for solving the elasticity equation in systems with strong elastic inhomogeneity. The key idea of the iterative-perturbation scheme is to split the inhomogeneous part of the elastic modulus tensor to the right-hand side of (6.18), thus transforming the inhomogeneous (possibly degenerate) elasticity problem to iterations of homogeneous (non-degenerate) systems. The nth iteration of the scheme reads

\[ \lambda^0_{ijkl} \frac{\partial^2}{\partial x_j \partial x_l} u_k^n(x) = \frac{\partial}{\partial x_j} \left[ \lambda^0_{ijkl} + \lambda'_{ijkl} \delta c(x) \right] (\varepsilon^0_{kl}(x) - \bar{\varepsilon}_{ij}) - \lambda'_{ijkl} \frac{\partial}{\partial x_j} \left[ \delta c(x) \frac{\partial u_k^{n-1}(x)}{\partial x_l} \right]. \]

(6.19)

In [74], rigorous justification for the formulation of the diffuse-interface model and the numerical scheme have been provided, and several numerical tests were performed to confirm the validity and the efficiency of the method.
6.3.2.3 Coupling with the phase field simulation

The main goal of solving the elasticity equations is to obtain the elasticity energy needed to predict the critical nucleus in the phase field model. The total free energy includes bulk chemical free energy, interfacial energy and inhomogeneous elastic energy

$$\Delta E_{\text{total}}(c) = \int_{\Omega} \left( \delta f(c) + \frac{\kappa}{2} (\nabla c(x,t))^2 + \frac{1}{2} \lambda_{ijkl}(x,t) \varepsilon_{ij}^{el}(x,t) \varepsilon_{kl}^{el}(x,t) \right) dx \quad (6.20)$$

where $\delta f(c)$ is the chemical free energy density of the solid solution, $\kappa$ is the gradient energy coefficient which is determined by the interfacial energy and thickness. The third term in (6.20) is the elastic energy given by

$$E_{\text{el}} = \frac{1}{2} \lambda_{ijkl} \varepsilon_{ij}^{el} \varepsilon_{kl}^{el} = \frac{1}{2} \left[ \lambda_{ijkl}^0 + \lambda_{ijkl}^r \delta c(x) \right] \left[ \varepsilon_{ij} + \delta \varepsilon_{ij} - \varepsilon_{ij}^c(x) - \varepsilon_{ij}^{\text{def}}(x) \right] \left[ \varepsilon_{kl} + \delta \varepsilon_{kl} - \varepsilon_{kl}^c(x) - \varepsilon_{kl}^{\text{def}}(x) \right].$$

In the future work, we will first apply the iterative-perturbation scheme coupled with the semi-implicit Fourier-spectral method for the phase-field model to compute the elastic energy, and then use the constrained string method in Chapter 5 to predict both critical nucleus and equilibrium state simultaneously.

6.3.3 Heterogeneous nucleation in solid states

Heterogeneous nucleation is an important but very complex phenomenon in solids. It has long been recognized that structural defects such as dislocations play a critical role in diffusional processes and phase transformations in solids.

Hu and Chen proposed a diffuse-interface model to describe diffusional processes in coherent systems with arbitrary microstructures and arbitrary spatial distribution of structural defects such as dislocations [38]. Hu et al incorporated the solute diffusion into the phase field model of dislocation dynamics combining the static and dynamic models [39].

Our main object is to use the phase field model to compute the heterogeneous nucleation such as dislocation. We will invest the morphology of critical nucleus at a single dislocation in solid state, and study the effect of the heterogeneous
elasticity on both critical nucleus and equilibrium precipitate.

6.3.3.1 Elastic field of a dislocation

We consider a simple binary solid solution with a compositional inhomogeneity described by \( c(x) \). For structure defects such as point defects, dislocations, twin and grain boundaries, cracks, and inhomogeneous inclusions, their spatial distributions can also be described by stress-free strains or eigenstrains \( \varepsilon_{ij}^d(x) \).

Let us use \( \varepsilon_{ij}(x) \) to denote the total strain measured with respect to the homogeneous solution with composition \( c_0 \). The Hooke’s law gives the local elastic stress,

\[
\sigma_{ij}^l = \lambda_{ijkl}(\varepsilon_{kl}(x) - \varepsilon_{kl}^0(x) - \varepsilon_{kl}^d(x)).
\]

Then we can calculate the equilibrium elastic field for an elastically inhomogeneous solid by solving the mechanical equilibrium equation. So the total elastic energy is given by

\[
E_{\text{elastic}} = \frac{1}{2} \int \lambda_{ijkl} \varepsilon_{ij}^l \varepsilon_{kl}^l \, dx
\]

where \( \varepsilon_{ij}^l = \varepsilon_{ij}(x) - \varepsilon_{ij}^0(x) - \varepsilon_{ij}^d(x) \).

To obtain the stress field around a single dislocation in the absence of compositional inhomogeneity, we consider an edge dislocation line lying along the [001] direction and passing through the origin with a Burger’s vector \( b = (0, b_0, 0) \). According to [55], the eigenstrain for such a dislocation is given by,

\[
\varepsilon_{22}^d(x) = b_0 \delta(x_2) H(x_1)
\]

(6.21)

where \( \delta(x_2) \) is the Dirac delta function and \( H(x_1) \) is the Heaviside step function.

The main problem of directly using equation (6.21) is the fact that the corresponding stress distributions show significant oscillations [38]. To get rid of the oscillations in the stress field, one solution to the boundary incompatibility is to introduce dislocation loops on discrete lattice points. Another way to reduce the oscillations in the dislocation stress field is to describe a dislocation using a spatial distribution of an infinite number of infinitesimal dislocations. In particular, one can use Gaussian functions to describe the Burger’s vector distribution of the
infinitesimal dislocations,

\[ b_i(x_1, x_2) = b_{i0} \frac{\alpha_1 \alpha_2}{\pi} e^{-|\alpha_1^2(x_1-x_1^0)^2+\alpha_2^2(x_2-x_2^0)^2|} \]

where \((x_1^0, x_2^0)\) is the center of the distribution, \(\alpha_1, \alpha_2\) are coefficients which determine the degree of spatial localization of the dislocation distribution, \(b_{i0}\) is the component of the entire burgers vector content of the dislocation. For example, for an edge dislocation with Burger’s vector \(b = (0, b_0, 0)\) along the \(z\) direction, the corresponding eigenstrain tensor can be written as

\[ \epsilon_{22}^d(x_1, x_2) = \frac{b_0 \alpha_1 \alpha_2}{\pi} \int \int e^{-|\alpha_1^2(x_1-x_1^0)^2+\alpha_2^2(x_2-x_2^0)^2|} \delta(x_2 - \bar{x}_2) H(x_1 - \bar{x}_1) d\bar{x}_1 d\bar{x}_2 \] (6.22)

### 6.3.3.2 Phase field description of a binary system with dislocation

To examine the nucleation and growth of a coherent precipitate near a dislocation, we use a spatial composition distribution \(c(x)\) to describe a binary system in solid state. The total free energy includes the chemical free energy which consists of both the local bulk free energy of a binary solution and the composition gradient energy, and elastic energy associated with solutes, defects and applied stresses.

\[ \Delta E_{\text{total}}(c) = \int_\Omega \left( \delta f(c) + \frac{\kappa}{2} (\nabla c(x,t))^2 \right) dx + E_{\text{elastic}} \] (6.23)

which is subject to the constraint for the average composition \(c_0\)

\[ \int (c(x) - c_0) dx = 0 \]

Then, the computation of critical nuclei and the Minimum Energy Path corresponding to the energy functional (6.23) could be done through the constrained string method [81]. We use a string to describe the most probable transition path between two metastable regions in configuration space. The Minimum Energy Path is computed through an evolution process, namely, if \(\varphi(\alpha,t)\) refers to the instantaneous position of the string, which corresponds to a composition profile,
then the string method is based on the solution of the following dynamic equation

\[ \varphi_t = -\left(\frac{\delta E_{\text{total}}(\varphi)}{\delta \varphi}\right)^\perp + \lambda \hat{\tau}. \]  \hspace{1cm} (6.24)

where \( \hat{\tau} \) is the unit tangent vector of the curve \( \varphi \), and the scalar field \( \lambda \) is a Lagrange multiplier.

We will discretize the string evolution equations in time using various semi-implicit schemes and time splitting schemes and apply the augmented Lagrange multiplier formulation to enforce the constraint which was discussed in Chapter 4. We will also invest the effect of a single dislocation on both critical nucleus and equilibrium one, and then extend the simulation in phase field models for more complicated dislocation systems.

### 6.3.4 Summary

Overall, my research in the computational materials science, jointly with mathematicians and materials scientists, gave me a valuable opportunity to develop my modeling, computational, analytical and communication skills, at the same time it helped to broaden my knowledge base in mathematics, physics and other related subjects. The methods and tools used in our works may also be applicable to a large class of biological, chemical and physical applications. These issues have recently started to play an increasing role in my research. While I am interested in continuing past works, I also look forward to taking on new challenges in the future.
Bibliography


Wolverton, C., First-principles prediction of equilibrium precipitate shapes in Al-Cu alloys; 1999. 79(9): p. 683-690


Vita
Lei Zhang

Lei Zhang was born in Yanji in the Jilin Province of China in 1978. He is the youngest child in his family. After completing his study at Changchun City Experimental High School, he went to the Peking University, China in 1997, where he studied Mathematics and received his Bachelors degrees in July 2001. From Sep. 2001 to Dec. 2003, he was studying at Academy of Mathematics and Systems Science, Chinese Academic of Science and got his Master degree of Mathematics.

In March 2004, he enrolled in the Ph.D. program in Mathematics at Pennsylvania State University to study Applied and Computational Mathematics under the supervision of Prof. Qiang Du.

His current research interest is in the fields of applied mathematics and numerical analysis. His work at Penn State involves the numerical algorithms, scientific computation and its application in materials science.